Synthesis, Spectroscopic Characterization and pH Dependent Electrochemical Fate of Two Non-Ionic Surfactants

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Two new nonionic surfactants; 1-sec-butyl-3-dodecanoylthiourea (DTU) and 1-dodecanoyl-3-phenylthiourea (DPTU) were synthesized and characterized by 1H NMR, 13C NMR and FTIR and UV-Vis spectroscopy. The detailed electrochemical fate of DTU and DPTU was investigated in a wide pH range of 2-12 by employing three electroanalytical techniques. The voltammetric signatures of the analytes showed a single irreversible anodic peak followed by two reversible peaks of the oxidation product. The irreversible behavior of the oxidation process was witnessed by the unequal components of total current in square wave voltammetry and scan rate based deviation of peak potential. The involvement of protons accompanying the electron transfer processes was ascertained from peak potential versus pH plots. Critical micelle concentration and hydrophilic-lipophilic balance of the synthesized surfactants were determined for the assessment of their cleaning, wetting and emulsifying properties.

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Some detergents and surfactants have been restricted and prohibited in the developed countries due to adverse environmental consequences. The manufacturers are now trying to synthesize environmentally friendly surfactants according to the environmental protection laws. With these facts in mind, we synthesized thiourea based surfactants which are expected to increase the fertility of the soil if their washed water is directed toward agricultural fields.

Surfactants are classified as ionics, nonionics and zwitter-ions. The demand and consumption of ionic surfactants were greater than nonionics in the mid of 19 century but now the market share of nonionic surfactants has reached to 40% of the total worldwide surfactants production. Nonionic surfactants excel other types due to their neutral behavior, compatibility with ionic surfactants and capability of forming complex mixtures as found in many commercial products. Nonionic surfactants excel as excellent solubilizing agents due to their very low critical micelle concentration. Such surfactants can work even in hard water as they do not yield ions in aqueous solution and hence, less or almost insensitive to electrolytes. Due to their neutral behavior, nonionic surfactants are non or less toxic than ionic surfactants and hence find use in cosmetics, pharmaceuticals and food products. They can also be used as wetting agents, emulsifiers and detergents.

Nowadays nonionic surfactants are in constant use in different varieties of domestic and industrial products. Prompted by the peculiar characteristics of non-ionic surfactants such as very low critical micelle concentration, insensitivity to hard water, no or low toxicity, low cost and compatibility with ionic surfactants, we synthesized and spectroscopically characterized more effective candidates of this class in high yield using the protocol reported in our recent article. Moreover, the oxygen, nitrogen and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities. Hence, the excellent metal ions complexation ability of our synthesized surfactants is expected to help the removal of toxic metals from polluted water.

Thiourea and its derivatives are used in a variety of industrial applications such as rubber vulcanization, electrodeposition and production of industrial cleaning agents. The properties of surfactants are envisioned to enhance by the incorporation of thiourea functionality. Hence, stimulated by the broad range applications of compounds containing thiourea functionality we synthesized and characterized two novel non-ionic thiourea containing surfactants, 1-sec-butyl-3-dodecanoylthiourea (DTU) and 1-dodecanoyl-3-phenylthiourea (DPTU). The lack of cost effective protocols for the synthesis of electroactive surfactants from commonly available chemicals, insufficient information about the fundamental electrochemistry of thiourea based surfactants and dearth of literature about the electrochemical fate of these surfactants prompted us to investigate the redox behavior of two electroactive members of this class of surfactants in a wide pH range using three electroanalytical techniques.

Experimental

Chemicals and general methods.— Lauryl chloride (98%), potassium thiocyanate (99%) and different aliphatic and aromatic primary and secondary amines (98%) were purchased from Sigma Aldrich. Fresh analytical grade dry acetone was used as solvent and dried before experiment. The products were purified by thin layer chromatography. NMR spectra were recorded on Bruker AC Spectrometers at 300.13 MHz for 1H and 75.47 MHz for 13C. Thermo nicollet-6700 spectrophotometer was used for FTIR characterization.

Synthesis of the compounds.— For the synthesis of DTU, 0.6 g potassium thiocyanate was dissolved in 50 mL dry acetone and introduced into 250 mL round bottom flask followed by the addition of 1.5 mL lauryl chloride. After heating for about 40 minutes, 2-butyl amine was added and kept the solution on stirring for 10-12 hrs. The product collected on condensing ice was washed for the removal of impurities with doubly distilled water. DPTU was synthesized by the same method using aniline instead of 2-butyl amine. The synthetic method can be seen in Scheme 1. The pure products of DTU and DPTU in 80 and 83% yield were obtained as white powder with melting points of 70 and 93°C respectively. The purity of the compounds was ascertained by 1H NMR, 13C NMR and FTIR spectroscopy. The spectral details of the compounds are given below:

(i) Spectral details of DTU

1H NMR (300 MHz, CDCl3 δ ppm): 0.86-0.96 (6H, m, 2CH3), 1.11-1.13 (3H, t, CH3-JH-H-JH= 6Hz), 1.26-2.34 (24H, m, 12CH2), 8.57 (1H, s, 3NH), 10.43 (1H, s, 3NH) 13C NMR 75.47 MHz CDCl3 δ ppm: 20.9 (C1, C4, C17), 22.7-37.2 (C2, C8-17), 53.0 (C3), 172.4 (C5).

(ii) Spectral details of DPTU

1H NMR (300 MHz, CDCl3 δ ppm): 0.87-0.92 (3H, t, CH3), 1.09-1.34 (7H, t, CH3-JH-H-JH= 7Hz), 1.12-1.34 (18H, m, 9CH2), 2.38-2.43 (2H, t, CH2.

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Materials and reagents.— For voltammetric analysis, 2 mM stock solutions of the synthesized compounds were prepared in ethanol and stored at 4°C. Fresh working solutions were prepared in 50% ethanol and 50% supporting electrolyte. Britton Robinson buffer was used as supporting electrolyte. For pH measurements INOLAB pH meter with Model no pH 720 was used. Microvolume measurements were done by EP-10 and EP-100 Plus Motorized Microliter Pipettes (Rainin Instrument Co. Inc., MA, USA).

Equipments and conditions for electrochemical experiments.— Voltammetric experiments were performed using µAutolab running with GPES 4.9 software, Eco-Chemie, The Netherlands. A glassy carbon (GC) was used as working electrode. Pt wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes. Before every experiment, the surface of GCE was polished with diamond spray (particle size 1 μm) followed by thorough rinsing with distilled water. All electrochemical experiments were conducted in a high purity nitrogen atmosphere at room temperature (25 ± 1°C). Differential pulse voltammetric experiments were carried out at 5 mV s⁻¹ scan rate. In square wave voltammetry (SWV) an effective scan rate of 100 mV s⁻¹ was used by setting the experimental conditions of 50 Hz frequency and 2 mV potential increments. For obtaining reproducible experimental results, the polished working electrode was used to place in the desired solvent followed by recording various differential pulse voltammograms until the achievement of a steady state baseline.

Results and Discussion

Structural characterization.— The formation of DTU and DPTU was ensured by the presence of stretches corresponding to C=O, C=–S, N–H and sp³ C–H in the FT-IR spectra. The presence of characteristic stretching vibrations of phenyl ring in the FT-IR spectrum of DPTU and its absence in DTU distinguished the structures of the synthesized compounds. In the proton NMR spectrum, a triplet due to CH₃ of the long chain further confirmed the formation of the desired surfactants. The proton NMR spectra of both surfactants were differentiated by the alkyl and aryl group of the amine attached to surfactant head group. Moreover, the presence of expected resonance for carbons in ¹³C-NMR spectra of DTU and DPTU also confirmed the successful synthesis of the designed surfactants.

Cyclic voltammetry.— Cyclic voltammery of 1 mM solution of both surfactants was first carried out between the potential limits of ±1.5 V at a sweep rate of 100 mV s⁻¹. During voltammetric experiments a constant flux of N₂ was kept over the solution surface in order to avoid the mixing of atmospheric oxygen into the solution. Based upon the initial experiments, a suitable potential window was set for capturing the overall electrochemical signature of the analytes. Cyclic voltammograms shown in Fig. 1 indicate the oxidation of DTU and DPTU at 0.81 and 0.46 V. In the reverse scan, two reduction peaks, c₁ and c₂ can be seen in the CV of DTU and only one in case of DPTU. The second scan voltammograms indicate the reduction peaks to be of reversible nature. On the basis of redox peaks at a potential very close to 0.0 V, the oxidation products of DTU and DPTU can be used as redox probes for the designing of electrochemical biosensors, and for the investigation of interactions between molecules/ions.

Cyclic voltammograms of 1 mM solutions of DTU and DPTU shown in Fig. 2 were recorded at various scan rates ranging from 10 - 500 mVs⁻¹. A slight positive shift of peak a₁, with increase in scan rate indicates the irreversible nature of oxidation process. The absence of corresponding peak of a₁ in the reverse scan also witnesses the irreversible nature of the oxidation process. No shift in the peaks offers evidence about their reversible nature. Eₚ-Eₚ/₂ values of about 60 mV further ensure their reversible character. The straight line plots of peak current versus square root of scan rate (Fig. 3) with zero intercept are consistent with the diffusion limited processes. The plots of log Iₚ vs. log v with slopes of 0.61 and 0.63 close to the theoretical value of 0.5 for a fully diffusion controlled process also support the oxidation processes to be mainly controlled by diffusion. However, the oxidation peaks of the products of DTU are controlled by partial adsorption and partial diffusion as witnessed from the slopes of log Iₚ vs. log v plots (Fig. 4). The contribution of adsorption is also evident from the comparatively sharp peaks of the oxidation products than the oxidation signal of DTU. The sharpness of these peaks is related to the fact that electron transfer occurs after the adsorption of analyte during an adsorption-controlled process while the broadness of the oxidation peaks of surfactants demonstrates the diffusion mode of transport.

Differential pulse voltammetry.— Differential pulse voltammograms (DPVs) of 1 mM surfactants in media of pH 2 - 12 were recorded for the determination of number of electrons and protons involved in their redox processes. Like CV, 1ˢᵗ and 2ⁿᵈ scan DPVs of DTU were also obtained as shown in Fig. 5. The width at half peak

Scheme 1. Synthesis of DTU and DPTU.

Figure 1. 1ˢᵗ and 2ⁿᵈ scan CVs of 1 mM DTU (A) and DPTU (B) obtained in pH 2 and 7.4 at 100 mV s⁻¹.
Figure 2. (A) 2nd scan CVs of 1 mM (A) DTU and (B) DPTU at different scan rates.

height ($W_{1/2}$) of peak $a_1$ with a value of 155 mV much greater than the theoretical value of 90.4 mV $^{24}$ for one electron redox process can be related to the possible overlapping of two, one electron transfer oxidation peaks. This oxidation peak shifts to more negative potentials with increase in pH of the medium. This behaviour is consistent with the comparatively facile electron abstraction in basic conditions as expected. In the 2nd scan of DTU obtained without cleaning the electrode surface, two product peaks $a_2$ and $a_3$ were obtained with $W_{1/2}$ values corresponding to the abstraction of one electron in each step. The shift in the location of these peaks with increasing pH of the medium shows the involvement of protons during electron transfer processes. Peak $a_2$ was found to merge with $a_3$ at pH higher than 9.0. Like anodic peaks, three cathodic peaks also appeared during the reduction of DTU and peak $c_2$ was found to combine with $c_3$ at pH higher than 6. Like DTU, DPTU also showed large $W_{1/2}$ value of the oxidation signal due to possible combination of two peaks. Moreover, the product signal was found to split in highly acidic conditions (Fig. 6) thus supporting our attribution of peaks overlapping in alkaline media.

Figure 3. Plots of anodic peak currents of DTU (A) and DPTU (B) vs. $\nu^{1/2}$ using CV data of Fig. 2.

Figure 4. Plots of log $I_{pa}$ vs. log $\nu$ using Fig. 2 data of DTU (A) and DPTU (B).

Figure 5. (A) 1st and (B) 2nd scan DPVs showing oxidation of 1 mM DTU at 5 mV s$^{-1}$ in different supporting electrolytes of pH 2 to 12 using Britton Robinson buffer (C) Plots of (■) $E_{pa2}$ and (●) $E_{pa3}$ vs. pH.
For the determination of number of protons involved in the redox processes peak potentials were plotted as a function of pH. For signal a1, a Nernstian slope of 60 mV/pH suggested the oxidation of DTU to occur by the involvement of equal number of electrons and protons. The same behaviour was also witnessed for the oxidation of DPTU. Plots of $E_p$ vs pH of all other peaks (Fig. 6.) showed slope values in very good agreement with Nernstian assessment for equal participation of electrons and protons. These results helped in proposing the pH dependent redox mechanistic pathways of DTU and DPTU.

**Square wave voltammetry (SWV).**—In SWV, the current is recorded in both positive and negative going pulses, so anodic and cathodic peaks of the electroactive species can be recorded in the same experiment. In comparison to CV and DPV, SWV is more advantageous owing to its ability of quickly measuring forward, backward and total current in one only scan. The reversible, quasi-reversible, and irreversible nature of the redox processes can be easily verified by using SWV. Successive SW voltammograms of 1 mM DTU and DPTU recorded in pH 7.4 are presented in Figs. 7A and 7B. The results complement well with the CV and DPV results. The absence of peaks a2 and a3 in the first scan and their appearance in 2nd scan indicates these signals to correspond to the oxidation of the reduction products of DTU and DPTU. The 2nd scan SWVs (Figs. 7C and 7D) showing forward and backward current components of the total current of DTU and DPTU were obtained to comment on the nature of the redox processes. The same direction of peaks and unequal currents of forward and reverse components of peak a1 justify the irreversible nature of oxidation corresponding to this signal. While the reversible nature of a2 and a3 is evident from the equal peak current intensities of both components of the total current.

**Proposed redox mechanism.**—The results of voltammetric experiments revealed the oxidation of DTU to occur in two-steps each involving the removal of $1e^-$. The proton coupled electron loss is suggested to occur from the amine attached to carbonyl group owing to its greater electron donating effect and higher ability of electron abstraction as compared to the other amine attached to secondary butyl group. The diamine radical is expected to stabilize by dimerization into a six membered ring. The results reveal the oxidation product to exhibit reversible two steps redox behavior. In the first step, amine group attached to secondary butyl and in the second step amine linked to carbonyl group are suggested to reduce as shown in Scheme 2. These mechanistic pathways are expected to encourage the synthetic organic chemists to seriously ponder over the use of electrochemical techniques for solving synthetic problems and transformation of compounds which cannot be achieved by traditional organic methods.

![Scheme 2](image-url)  
**Scheme 2.** Proposed redox mechanism of DTU.
**Scheme 3.** Proposed Redox mechanism of DPTU.

_UV-Vis spectroscopy._—UV-Vis spectroscopy was employed for the determination of CMC of both surfactants. The electronic absorption spectra of DTU and DPTU have been presented in Fig. 8A and 8B. DTU shows a single peak at 270 nm due to $\pi \rightarrow \pi^*$ transition of carbonyl group while DPTU gives two peaks at 248 and 298 nm due to $\pi \rightarrow \pi^*$ transition of phenyl and carbonyl groups respectively as reported for such functional groups in literature.\(^{27,28}\) A small peak at 221 nm also appears due to possible $n \rightarrow \sigma^*$ transition of the carbonyl group.

The CMCs of both surfactants was determined from the intersection of the two linear segments of the plots of absorbance versus concentration (Fig. 8C and 8D). The greater slope of the first linear segment than the second can be related to the presence of only monomers in the sample solution (at concentration lower than CMC) whose absorption increases with increase in their concentration. At concentration $\geq$ CMC, micelles form in the solution and only their number gets increased with further increase in surfactant concentration. In micelles the chromophores of the surfactant molecules get entrapped and hence less exposed to light. Therefore, the absorbance due to increase in micelles does not increase as rapidly as monomers.\(^{29–31}\) The CMC of DTU and DPTU with values 15.31 and 15.73 $\mu$M were determined which are very close to the conductometrically and tensiometrically determined CMCs of nonionic surfactants.\(^1\) Such low CMCs are suggestive of high cleaning ability of these surfactants. Moreover,

**Figure 8.** (A, B) Absorption spectra of different concentrations of DTU and DPTU (C,D) Plots of absorbance vs. concentration for the evaluation of CMC of DTU and DPTU at 270 and 298 nm respectively.
Conclusions

Two new non-ionic surfactants 1-sec-butyl-3-dodecanoylthiourea (DTU) and 1-dodecanoyl-3-phenylthiourea (DPTU) were successfully synthesized in 80 and 83% yield by a facile method. Their pH dependent redox mechanistic pathways were proposed on the basis of results obtained from three electrochemical techniques. DPTU was found to oxidize in two irreversible one electron transfer steps following a cascade mechanism. The two steps oxidation occurred by the loss of one proton and one electron as evidenced from the Nernstian slope of $E_{pa}$ vs. pH plot. Similar electrochemical response was observed for DTU, and the same number of electrons and protons were found to involve in its two steps oxidation mechanism as witnessed by the large boost of half peak width in basic conditions. DPTU showed this merging up to slightly acidic conditions just below neutral pH. The studied thiourea based surfactants followed irreversible diffusion controlled oxidation processes. However, the oxidation products showed reversible adsorption controlled redox processes. The CMC and HLB values demonstrated excellent cleaning, wetting and emulsifying properties of the synthesized surfactants.

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