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ORIGINAL ARTICLE

Synthesis, Characterization and Investigation of Different Properties of Three Novel Thiourea-Based Non-ionic Surfactants

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Abstract Three novel thiourea-based non-ionic surfactants, 3-decanoyl-1,1-diphenylthiourea, 3-dodecanoyl-1,1-diphenylthiourea and 1,1-diphenyl-3-tetradecanoylthiourea were synthesized from carbonyl chlorides, potassium thiocyanate and amines in high yield. The synthesized compounds were characterized by different techniques like ^{1}H NMR, ^{13}C NMR, FTIR and UV-Visible spectrophotometry. These surfactants are soluble in nonpolar and polar organic solvents and resist solubility in water due to the presence of thiourea group. Electronic absorption spectroscopy was used to evaluate their critical micelle concentration (CMC) in different solvents. The CMC was found to decrease with increase in hydrophobic carbon chain length as expected. Moreover, the effect of pH on their spectral transition was investigated and the two peaks were found to merge in highly alkaline conditions.

Keywords Synthesis · Non-ionic surfactants · Critical micelle concentration · pH effect · Hydrophobic character

Introduction

Non-ionic surfactants (NIS) have broad range applications in industries, agriculture, cosmetics, food, paints and drugs [1–5]. NIS are not dissociated in aqueous solution due to the unavailability of an ionizable moiety in their structure. The dispersion capability of such surfactants increases with increasing chain length. Non-ionic surfactants are used as excellent solubilizing agents due to their very low critical micelle concentration [6–9]. Manufacturers are paying the utmost attention to such surfactants due to their non toxicity, low cost and compatibility with ionic surfactants [10–14]. Thus, spurred on by the peculiar characteristics and wide applications of non-ionic surfactants, scientists have sought new methods for the synthesis of other more effective candidates of this class in high yield. Some NIS can act as excellent ligands for complexation with metals and thus such surfactants offer opportunities to the environmentalists for the safe removal of toxic metals from polluted water. Surfactants with an amine group have appreciable water solubility and thus find use in hand washing products and liquid soaps with favorable skin effects [15–17]. Keeping cost affectivity, environmental friendliness, compatibility and extensive applications of non-ionic surfactant in consideration, we synthesized and characterized three new thiourea-based NIS using common laboratory materials as illustrated in Schemes 1 and 2. The method used is harmless and easy to handle. The objectives of this work are to draw the attention researchers towards these novel thiourea-based non-ionic surfactants and to emphasize the hidden aspects for further study.

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Experimental

Chemicals, Instruments and Methods

Lauryl chloride (98 %), potassium thiocyanate (99 %), different aliphatic and aromatic primary and secondary amines (98 %) were purchased from Sigma Aldrich. Fresh analytical grade dry acetone was used as the solvent and dried before experiments. The products were 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 was used for CMC determination and investigation of pH and solvent effects.

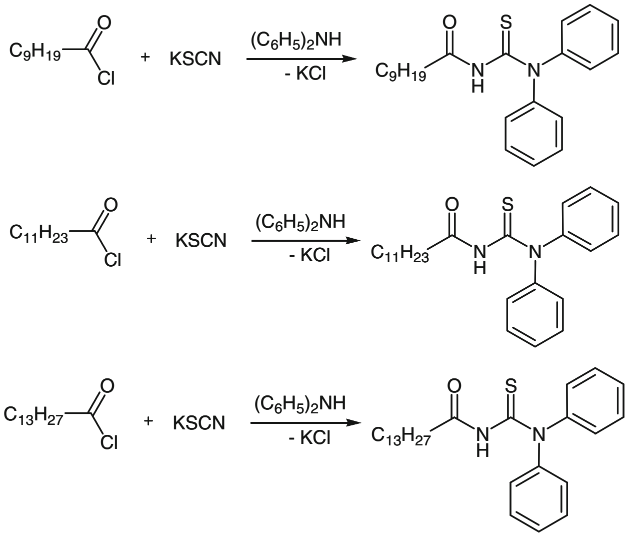
3-Decanoyl-1,1-diphenylthiourea

For the synthesis of 3-decanoyl-1,1-diphenylthiourea 0.709 g (0.00724 mol) potassium thiocyanate was dissolved in 50 mL dry acetone and introduced into a 250-mL round-bottom flask followed by the addition of 3 mL decanoyl chloride. Heating the solution for 40 minutes at 90 °C, 1.224 g diphenylamine was added and the solution was kept stirring for 12 hrs. Finally, the products collected on condensing in ice water were washed with doubly distilled water for the removal of impurities. The pure product with 78 % yield was obtained as a light yellow 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 ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy and the spectral details are given below:

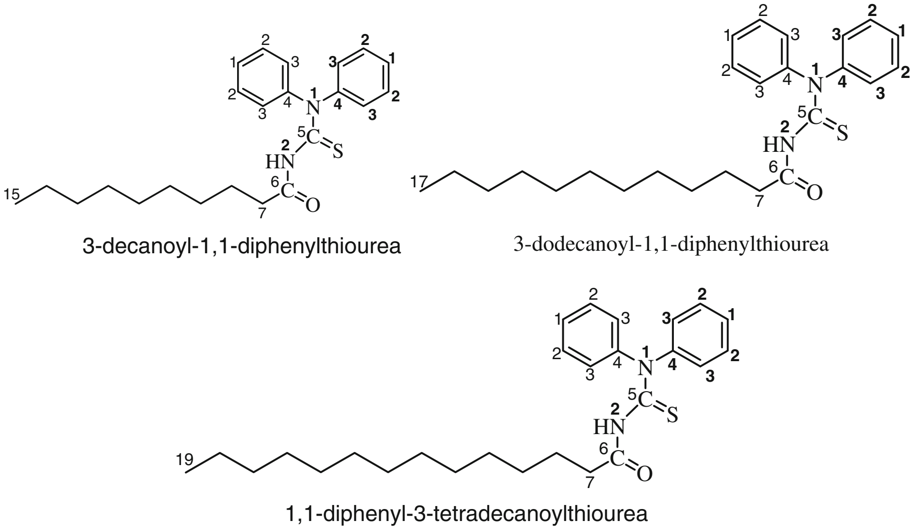
^{1}H NMR (300 MHz, CDCl$_3$, δ-ppm): 0.87–0.90 (3H, t, CH$_3$, ^3J [^{1}H,^{1}H] = 7 Hz), 1.07–1.65 (14H, m,7CH$_2$), 2.26–2.36 (2H, t, CH$_2$. ^3J [^{1}H,^{1}H] = 7 Hz$_)$, 6.49–7.44 (10H,m, CH,) 8.72 (1H, s, ^{2}NH) ^{13}C NMR (75.5 MHz CDCl$_3$, δ-ppm): 14.1 (C$_{.15}$), 22.6–37.0 (C$_{7-14}$), 117.7–120.2 (C$_{1,1,3,3}$), 127.5–129.0 (C$_{2,2,2,2}$), 142.5 (C$_{,4,4}$), 169.6 (C$_6$), 182.0 (C$_5$). IR (υ cm^{-1}): 3268.5, 3156.3 (N-H), 3035.8 (Ar-H, C-H, sp^2), 2913.7, 2843.5, (sp^3, C-H), 1680.5 (CO).

3-Dodecanoyl-1,1-diphenylthiourea

For the synthesis of 3-dodecanoyl-1, 1-diphenylthiourea, 6.3 mmol potassium thiocyanate was dissolved in 50 mL



Scheme 2 Synthetic method for the preparation of non-ionic thiourea-based surfactants



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

dry acetone and introduced into a 250-mL round-bottom flask followed by the addition of 1.5 mL dodecanoyl chloride. After heating the solution for 40 minutes at 90 °C, 6.3 mmol diphenylamine was added and the solution kept stirring for about 12 hrs. The products were finally collected on condensing in ice water and washed with doubly distilled water to remove the impurities. The product with 83 % yield was obtained as a light yellow powder. The structure of the compound is shown in Scheme 1 and the stepwise preparation protocol can be seen in Scheme 2. The purity of the synthesized surfactant was ascertained by ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy. The spectral details of the compound are given below:

^{1}H NMR (300 MHz, $CDCl_3$, δ-ppm): 0.88-0.92 (3H, t, CH_3, ^3J [^{1}H,^{1}H] = 7 Hz), 1.35–1.57 (18H, m, 9CH_2), 2.23–2.56 (2H, t, CH_2. ^3J [^{1}H,^{1}H] = 7 Hz), 6.96–7.52 (10H,m, CH,) 8.53 (1H, s, ^{2}NH) ^{13}C NMR (75.5 MHz $CDCl_3$, δ-ppm): 14.2 (C_{17}), 22.3–36.4 (C_{7-16}), 119.7–120.2 ($C_{1,1,3,3}$), 127.2–129.6 ($C_{2,2,2,2}$), 140.5 ($C_{,4,4}$), 172.3 (C_6), 180.7 (C_5). IR (υ cm^{-1}): 3296.8, 3177.3 (N-H), 3048.5 (Ar-H, C-H,sp^2), 2916.2, 2849.5, (sp^3, C-H), 1690.3 (CO).

1,1-Diphenyl-3-tetradecanoylthiourea

For the synthesis of 1,1-diphenyl-3-tetradecanoylthiourea, 11.2 mmol potassium thiocyanate was dissolved in 50 mL

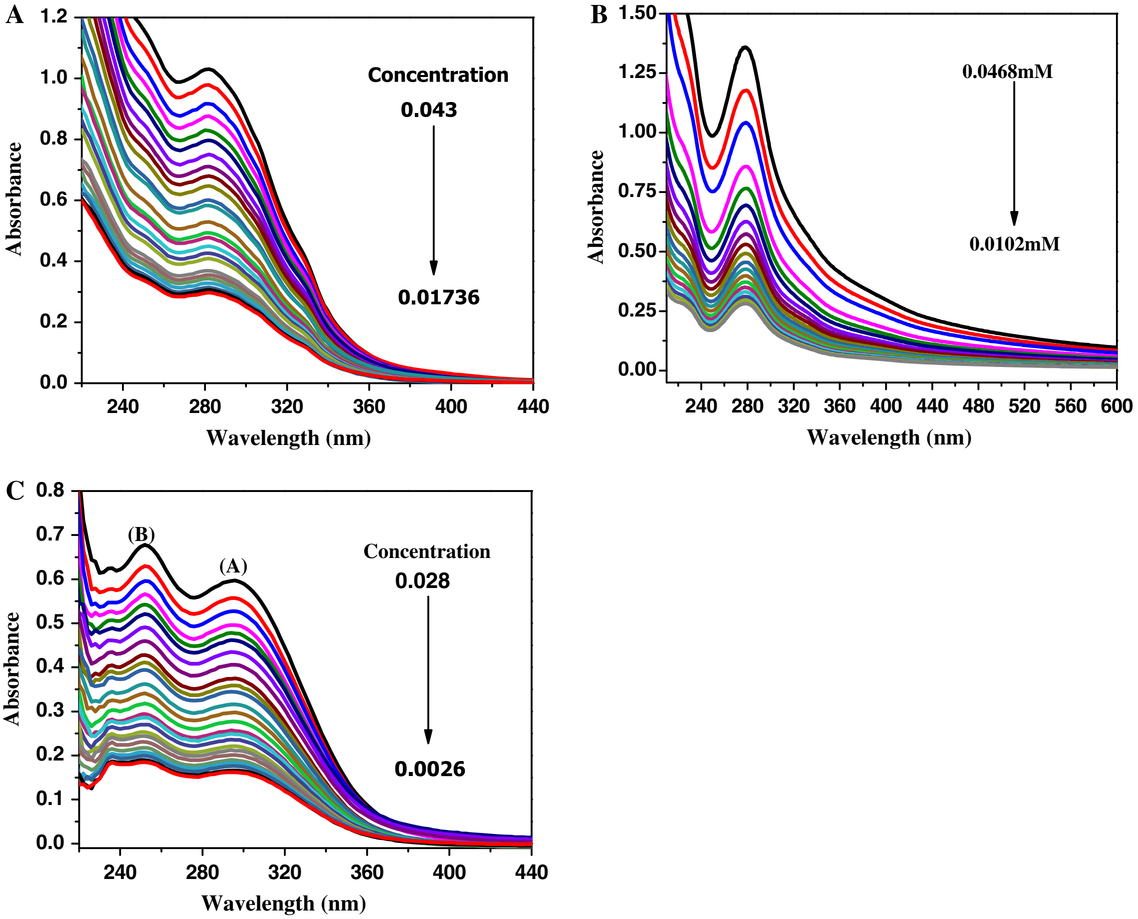


Fig. 1 UV-Vis spectra of 3-decanoyl-1,1-diphenylthiourea (**a**), 3-dodecanoyl-1, 1- diphenylthiourea (**b**) and 1, 1-diphenyl-3-tetradecanoylthiourea (**c**) in ethanol

Table 1 Physical properties of (**C_{10}**, **C_{12}** and **C_{14}**) non-ionic thiourea-based surfactants

Code	Mol. formula	Molecular mass	Color	mp (°C)	Solubility	CMC (mM)
C_{10}	$C_{23}H_{30}N_2SO$	382	Light yellow	50	Ethanol, methanol	0.023
C_{12}	$C_{25}H_{34}N_2SO$	410	Light yellow	78	Ethanol, methanol	0.013
C_{14}	$C_{27}H_{38}N_2SO$	438	Light yellow	87	Ethanol, methanol	0.009

dry acetone and introduced into a 250-mL round-bottom flask along with 3 mL tetradecanoyl chloride. After heating the solution at 90 °C for about 40 minutes, 1.9 g diphenylamine was added and the solution kept stirring for about 12 hrs. Finally, the products collected on condensing in ice water were washed with doubly distilled water for the removal of impurities. The pure product with 88 % yield was obtained as a light yellow powder. The structure of the compound is represented in Scheme 1 and the preparation method is given in scheme 2. The purity of the compound was ensured by ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy. The spectral details of the surfactant are given below:

^{1}H NMR (300 MHz, $CDCl_3$, δ-ppm): 0.88–0.92 (3H, t, CH_3, ^{3}J [^{1}H,^{1}H] = 7 Hz), 1.35–1.57 (18H, m, $9CH_2$), 2.23–2.56 (2H, t, CH_2. ^{3}J [^{1}H,^{1}H] = 7 Hz), 6.96–7.52 (10H,m, CH,) 8.53 (1H, s, ^{2}NH) ^{13}C NMR (75.5 MHz $CDCl_3$, δ-ppm): 14.1 (C_{19}), 22.7–37.1 (C_{7-18}), 117.7–120.9 ($C_{1,1,3,3,3,3}$), 127.0–129.3 ($C_{2,2,2,2}$), 145.3 ($C_{4,4}$), 169.5 (C_6), 181.8 (C_5). IR (υ cm^{-1}): 3235.7, 3183.0 (N–H), 3054.8 (Ar–H, C–H,sp^2), 2916.6, 2849.4, (sp^3, C–H), 1719.0 (CO).

Results and Discussion

The critical micelle concentration was assessed by UV-Visible spectrometry. The absorbance spectra were recorded over a wavelength range of 200–800 nm. The spectra of the synthesized three novel non-ionic thiourea based surfactants obtained at room temperature hare presented in Fig. 1a–c. The critical micelle concentration was determined by plotting absorbance versus concentration. In all cases, the plots presented two linear parts with different slopes and the critical micelle concentration was evaluated from their intersection. The CMC values obtained from the given UV-Visible data are listed in Table 1. The variation in the hydrophobic part was found to alter the critical micelle concentration of surfactants. The CMC values of thiourea-based novel non-ionic surfactants decreased with increases in the chain length of the carbons as documented in the literature [18–22]. These compounds synthesized by the reaction of diphenylamine showed different behaviors towards UV-Visible light and different pH media. The compound with a ten-carbon chain length gave a broad peak at 282 nm, a surfactant with a twelve-carbon chain gave a sharp peak whereas with fourteen carbons the compound registered two broad peaks at 250 nm and 294 nm in ethanol solvent. The CMC was calculated from absorbance versus concentrations plots as shown in Fig. 2. In pre-micellar region, the surfactants exist in monomeric forms which absorb more light as their chromophores are exposed. While in aggregates, the chromophores remain buried in micelles and thus get screened from UV-Vis light.

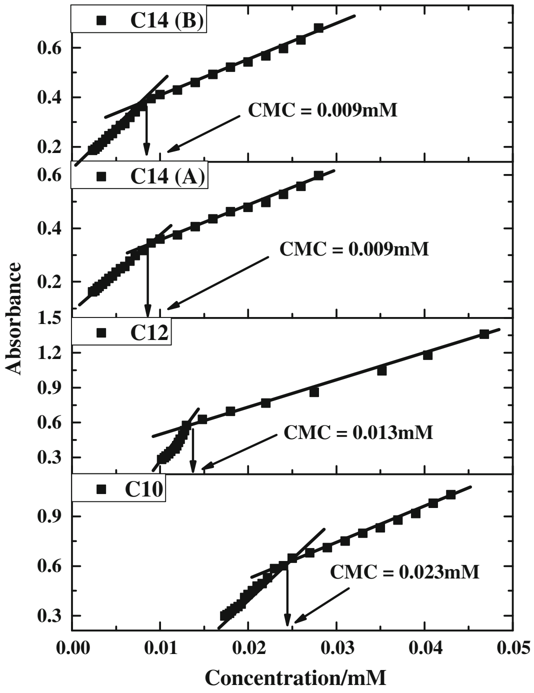


Fig. 2 Absorbance versus concentration plots of C_{10}, C_{12} and C_{14} compounds in ethanol

Table 2 CMC of (**C_{10}, C_{12}** and **C_{14}**) non-ionic thiourea-based surfactants in different solvents

Code	Ethanol	Methanol	50 % Water–ethanol mixture	50 % Water–methanol mixture
C_{10}	0.024	0.020	0.014	0.011
C_{12}	0.013	0.010	0.007	0.006
C_{14}	0.009	0.007	0.006	0.004

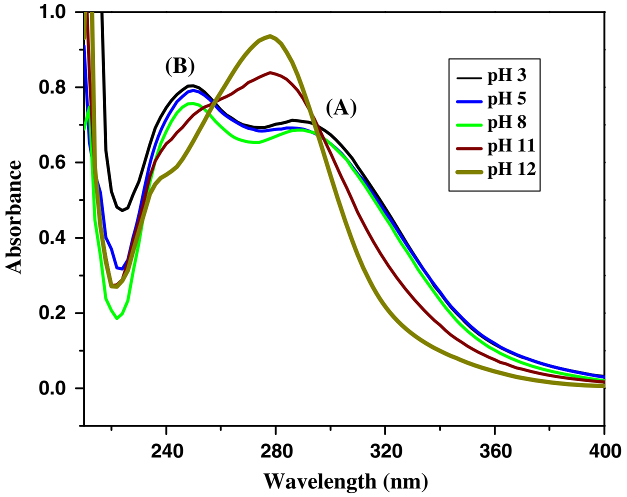


Fig. 3 UV-Vis spectrum of 1,1-diphenyl-3-tetradecanoylthiourea (C_{14}) obtained in different pH media

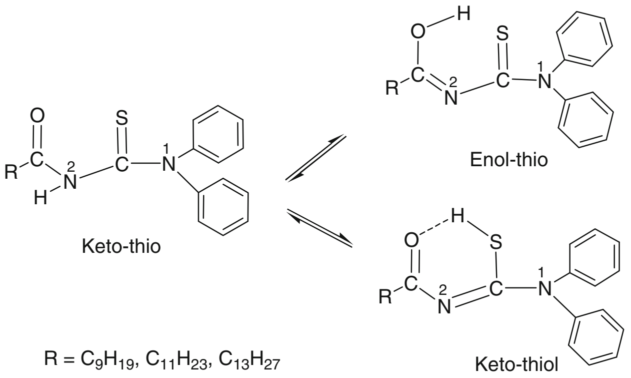
Hence, a lower increase in absorbance is evidenced in the post micellar segment of the plot as compared to the premicellar region.

The CMC of surfactants are pronouncedly influenced by changing the solvent due to variation in polarity and a corresponding alteration in solute- solvent interaction. The non-polar part of the surfactants experiences a greater hydrophobic effect with a concomitant decrease in CMC by increases in polarity of the solvent. The mixing of another solvent or co-solvent also alters the CMC of surfactant solution by a mechanism involving the penetration of one solvent into the micellar core of the surfactant solution. The study of our thio-based non-ionic surfactants in different solvents like methanol and 50 % water-ethanol mixture indicates the CMC to modulate with change in solvent system. The results of UV-Vis spectroscopic investigations reveal that the CMCs of these compounds in methanol, in 50 % a water-ethanol mixture and a 50 % water-methanol mixture became gradually lower with increasing solvent polarity as depicted in Table 2. An examination of Table 2 reveals that the increase in polarity of the solvent affects the CMC due to greater repulsion with the hydrophobic part of the compounds. The decrease in CMC of thio-based non-ionic surfactants with increasing polarity of the medium can be seen in Figs. S1–S4.

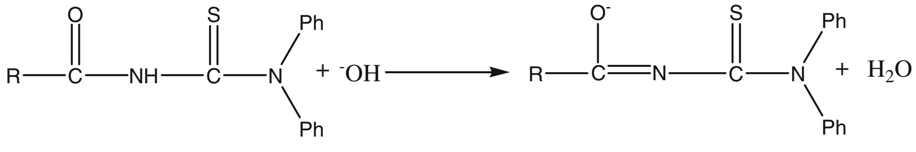
Thiourea-based non-ionic surfactants were also studied in different pH media to visualize their electronic absorption behavior in acidic, neutral and basic media. The effect of pH is shown in Figs. 3 and S-5. The results indicate that absorbance of A C-14 based surfactant becomes lower with a change in pH from 3 to 8 and the two peaks merge into a single peak (at pH 10) whose absorption intensity increases with a further rise in pH up to 11 and 12. In strongly alkaline conditions of pH 11–12, the narrowness and increase in peak intensity of all the three surfactants is attributed to the deprotonation of –NH group and a consequent increase in conjugation as shown in Scheme 3. The spectra of compounds with ten and twelve carbon chain lengths show a single peak at 282 nm where the fourteen carbon-containing compound absorbs at 250 nm and 294 nm. All the three surfactants have the same conjugated hydrophilic moiety so these should give the same spectral signature. However, unlike C-10- and C-12-based surfactants, the UV-Vis spectrum of the C-14 surfactant gives a second peak which may be due to its existence in such a geometric structure which could undergo an electronic absorption transition at two wavelengths. The pH study also reflects the most interesting phenomenon is the presence of two isosbestic points in the spectra. It is due to the keto-thiol and enol-thio tautameric forms as represented in Scheme 4. In these two, the OH in the enol-thio form is more easily depronated than the SH in keto-thiol forms and the sharpness of the peak is also related to the enol-thio form. A further pH study is in progress for getting useful insights into the indefinite aspects of thiourea-based non-ionic surfactants for improved and environmentally friendly applications.

Conclusions

Three novel non-ionic thiourea-based surfactants were successfully synthesized by a new method from simple raw materials available in the laboratory. The synthesized surfactants were well characterized by UV-Visible, FTIR, ^{1}H- and ^{13}C-nuclear magnetic resonance spectroscopy. These compounds can possibly be tailored appreciably under basic conditions as the results of the pH effect showed that such surfactants offer resistance to acid media. Electronic absorption spectroscopy was successfully employed for the evaluation of the critical micelle concentration of the synthesized surfactants from the intersection of the two linear segments of the plots of absorbance versus concentration. The solvent effect showed that the CMC is modulated by changing the polarity of the medium. The



Scheme 4 Tautomeric forms of non-ionic surfactants



R= C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$ Ph=C_6H_5

Scheme 3 Demonstration of the increase in volume of the chromophore of non-ionic surfactants under alkaline conditions leading to a more intense peak in UV-Vis spectra washing water of these non-ionic surfactants is expected to increase the fertility of soil by the provision of thiourea. As introduction of thiourea group in the structure of a surfactant lowers its solubility in water, so, further study is in progress to incorporate such moieties in thiourea-based non-ionic surfactants to improve their water solubility, cleaning action and biodegradability.

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