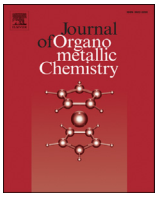
Journal of Organometallic Chemistry 819 (2016) 194–200

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



Study of new ferrocene-based thioureas as potential nonionic surfactants

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ARTICLE INFO

Article history:
Received 25 March 2016
Received in revised form
30 June 2016
Accepted 10 July 2016
Available online 14 July 2016

Keywords:
Ferrocene
Thioureas
Surfactants
CMC
Micelles
DFT
Redox potential

ABSTRACT

Three new thiourea based ferrocenyl surfactants i.e. 1-(decanoyl)-3-(4-ferrocenylphenyl) thiourea (**DP**), 1-(decanoyl)-3-(4-ferrocenyl-2-methylbenzyl) thiourea (**DMth**), 1-(decanoyl)-3-(3-ferrocenylphenyl) thiourea (**DM**) have been successfully synthesized and well characterized by various analytical techniques, such as FT-IR, ^{1}H and ^{13}C NMR, AAS and elemental analysis. Furthermore, the single crystal XRD analysis was done for **DP**. To evaluate their amphiphilic nature, their CMC was determined through UV–visible spectroscopy that varies between 0.05 mM and 0.5 mM. The **DP** compound possesses lower CMC, whereas **DM** has considerably higher CMC value. Cyclic voltammetric technique was used to determine their redox behavior around CMC as well as their redox potentials, which follow the same trend as that of CMC. The DFT calculated energies of HOMO and LUMO orbitals correlate well with the experimentally determined redox potentials.

1. Introduction

Surface properties of the surfactant systems can be changed by the addition of inorganic salts or cosurfactants but in new developments, many attempts have been made to introduce certain moieties into the surfactants structure that helps to control the formation of molecular assembly [1,2], by using wide variety of external stimuli such as pH [3], temperature change [4], photochemical [5] and redox reaction etc. [6,7]. These external stimuli with particular moieties such as ferrocene [8] and azo benzene [9] in surfactant structure can be applied to the micelles electrolysis. This approach of controlling the reversible formation of aggregates structure is also applicable to the controlled release of many enclosed substances such as drugs, genes and perfumes from the molecular assemblies [10–12].

Ferrocene owing a redox center, π-conjugated system, and an exclusive electron transfer ability which make it a potential candidate to be used as an electronic mediator in electrochemical and biosensor devices [13]. Ferrocene and its derivatives play an important role in the electron transfer between electrode and redox matrix. Moreover, its stability, hydrophobicity, non-toxicity and synthetic convenience have attracted the researcher's interest to employ it as a redox active group in surfactant systems. On the other hand, its oxidation states can be reversibly switched by using electrochemical methods that stimulate micelles assemblies of the surfactant system [14,15] which in turn drastically changes the solution properties [16].

A wide variety of ferrocene-based surfactants have been synthesized [17–27]. Development of these approaches lead to the formation of prominent assemblies such as liposomes, vesicles, liquid crystals, and nanostructures that have potential applications in biosensors, delivery system, microfluidic devices and interactions with bio-molecules [28–35]. In this article, we report the synthesis, characterization and critical micelles concentration of three novel ferrocene-based thioureas having nine hydrocarbon tail that can potentially act as nonionic surfactant. Some ferrocene incorporated thioureas, amides, selenoureas, and guanidines have been synthesized by our research group possessing antitumor and

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http://dx.doi.org/10.1016/j.jorganchem.2016.07.003
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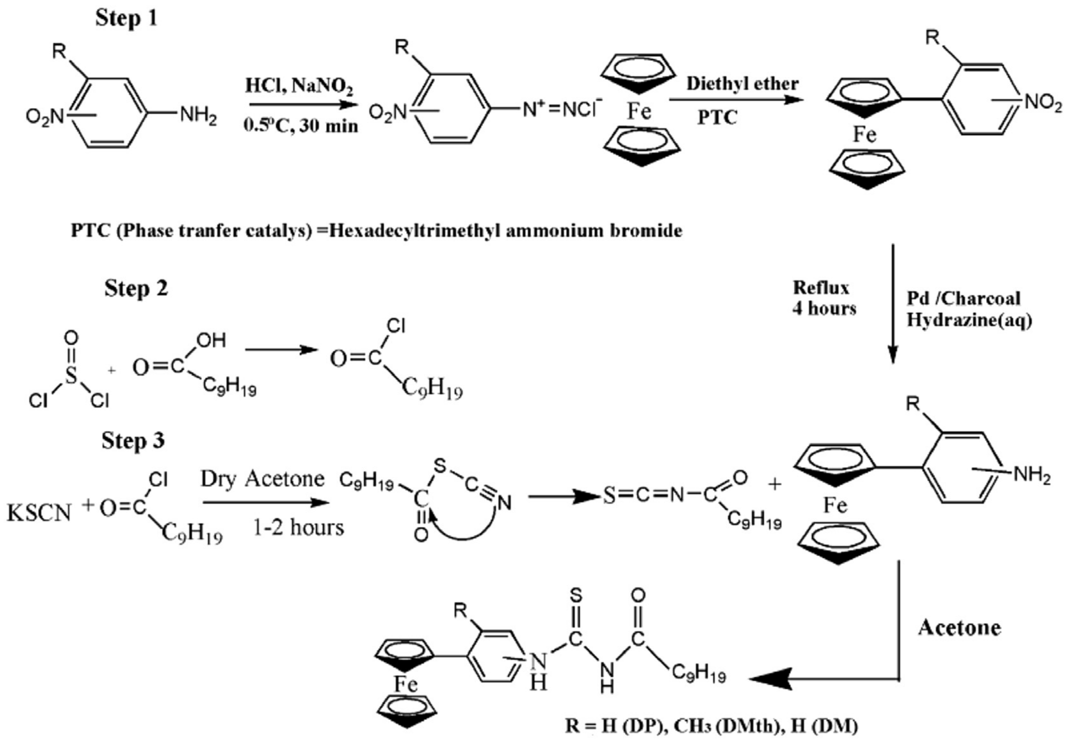

Scheme 1. Synthetic scheme for ferrocene incorporated thiourea based surfactants.

DNA binding activities [36–42]. Thioureas based cationic and nonionic surfactants have been reported with numerous applications in toxic metal extractions and biological activities [43–46]. Presence of long hydrocarbon chain developed the amphiphilic properties in ferrocene-based *N,N′*-disubstituted thioureas.

2. Experimental

2.1. Material and methods

Chemicals such as ferrocene, 3-nitroaniline, 4-nitroaniline, 2-methyl-4-nitroaniline, hydrochloric acid, sodium nitrite, hexadecyltrimethyl ammonium bromide, hydrazine, Pd-charcoal, KSCN, thionyl chloride and decanoyl chloride were purchased from Sigma Aldrich/Merck. All the solvents were dried, distilled and purified according to reported methods. ^{1}H and ^{13}C NMR spectra were taken on a Bruker 300 MHz spectrophotometer in chloroform and tetramethylsilane (TMS) was used as an internal reference. FT-IR data was recorded on a Thermoscientific NICOLET 6700 FT-IR instrument. Elemental analyses was done on LECO-932 CHNS analyzer and Perkin-Elmer Atomic Absorption Spectrometer model 2380 was used to determine Fe concentration.

2.1.1. General procedure for synthesis

The synthesis of ferrocene containing thioureas was done in three steps. In the first step *para*, *meta* and methyl derivatives of ferrocenyl aniline were synthesized by the method reported previously by our research group [39,42]. In the second step, the decanoic acid (2 ml, 10.37 mmol) was converted into its acid chloride by treating with $SOCl_2$ (0.7 ml, 10.3 mmol) [49]. In the third step, the distilled decanoyl chloride was dissolved in dry acetone under N_2 atmosphere. To this solution potassium thiocyanate was added in 1:1 M ratio to form the respective isothiocyanate. The reaction mixture was heated gently for 15 min and then stirred for 1–2 h. Afterwards, ferrocenyl aniline was added to the reaction mixture under an inert atmosphere and the suspension was allowed to stir for 4 h. The progress of the reaction was monitored by TLC after regular intervals. The reaction mixture was then poured into the ice cold water and stirred well. The solid product was filtered off and washed with deionized water. The product was dried in air and recrystallized in ethyl acetate (Scheme 1).

2.1.2. 1-(Decanoyl)-3-(4-ferrocenylphenyl) thiourea (DP)

Quantities used were 0.149 ml (0.72 mmol) decanoyl chloride, 0.07 g (0.72 mmol) potassium thiocyanate and 0.2 g (0.72 mmol) 4-ferrocenylaniline. **Yield 73%**, **FT-IR** (υ cm^{-1}): 488 (Fe-Cp), 3183 (NH), 1681 (C═O), 1104–1245 (C═S), 1455–1596 (C═C), 2918 (sp^2 CH). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 12.47 (s, 1H, CSNH), 9.02 (s, 1H, CONH), 7.62–7.52 (d, 4H, C_6H_4), 4.65 (s, 2H, C_5H_4), 4.35 (s, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.41 (s, 2H, C_9H_{19}), 1.72 (s, 2H, C_9H_{19}), 1.31 (m, 12H, C_9H_{19}), 0.91 (s, 3H, C_9H_{19}); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm): δ 177.7, 174.4, 138.2, 135.2, 126.3, 123.8, 84.5, 69.7, 69.1, 66.5, 37.4, 31.8, 29.4, 29.3, 29.2, 29.0, 24.8, 22.7, 14.1. **Elemental Analysis Calcd.** (%) for $C_{27}H_{34}FeN_2OS$: C, 66.13; H, 6.98; N, 5.72; S, 6.55; Fe, 11.38. Found (%): C, 66.20; H, 6.93; N, 5.78; S, 6.47; Fe, 11.44.

2.1.3. 1-(Decanoyl)-3-(4-ferrocenyl-2-methylbenzyl) thiourea (DMth)

Quantities used were 0.142 ml (0.68 mmol) decanoyl chloride, 0.06 g (0.68 mmol) potassium thiocyanate and 0.2 g (0.72 mmol) 2-methyl-4-ferrocenylaniline. **Yield 71%**, **FT-IR** (υ cm^{-1}): 488 (Fe-Cp), 3181 (NH), 1692 (C═O), 1196–1262 (C═S), 2916 (sp^2 CH), 2849 (sp^3 CH). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 12.37 (s, 1H, CSNH), 8.72 (s, 1H, CONH), 7.74–7.28 (d, 3H, C_6H_4), 4.50 (s, 2H, C_5H_4), 4.32 (s, 2H, C_5H_4), 4.16 (s, 5H, C_5H_5), 2.41 (s, 3H, $C_6H_3CH_3$, ppm), 1.77 (m, 2H, C_9H_{19}), 1.77–0.88 (m, 12H, C_9H_{19}), 0.91 (s, 3H, C_9H_{19}); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm): δ 177.6, 174.2, 136.2, 120.5, 120.9, 77.6, 69.8, 69.3, 68.1, 31.9, 29.7, 29.25, 29.0, 22.7, 14.1. **Elemental Analysis Calcd.** (%) for $C_{28}H_{38}FeN_2OS$: C, 66.39; H, 7.56; N, 5.53; S, 6.33, Fe, 11.03. Found (%): C, 66.27; H, 6.48; N, 5.21; S, 6.38, Fe, 10.95.