J Surfact Deterg
DOI 10.1007/s11743-013-1511-z

ORIGINAL ARTICLE

High Yield Synthesis, Detailed Spectroscopic Characterization and Electrochemical Fate of Novel Cationic Surfactants

**Imdad Ullah · Ahmad Naveed · Afzal Shah ·
Amin Badshah · Zia-ur-Rehman ·
Gul Shahzada Khan · Arif Nadeem**

Received: 16 March 2013 / Accepted: 9 July 2013

Abstract Two new cationic surfactants, *N*-(dodecanoyl(ethylammonio)carbonothioyl)-*N*-ethylbenzenaminium bromide and *N*-(dodecanoyl(ethylammonio)carbonothioyl)-*N*-ethyl-*N*-phenylbenzenaminium bromide were synthesized with a high yield by the reaction of appropriate amounts of lauryl chlorides, potassium thiocyanate, amine and alkyl halides. The structures were characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR and UV–Vis spectroscopy. Cyclic, square wave and differential pulse voltammetry were used to investigate the electrochemical fate of both surfactants over a wide pH range.

Keywords Synthesis · Spectroscopy · Isosbestic point · Redox mechanism · Cationic surfactants · Critical micelle concentration

Introduction

Surfactants play a key role in catalysis, coating, dispersion, electronic, flotation of minerals, lubrication, and retardation of evaporation from lakes and reservoirs. Many pharmaceutical products, e.g., skin lotion, ointments, birth control foams, etc. are being formulated and developed using principles and techniques of surface active compounds [1]. Surfactants are extensively used in the formulation of pesticides and herbicides [2]. The refined and unique properties of surfactants such as detergency, solubilization, and wetting phenomena find useful applications in various fields ranging from agriculture sprays to oil recovery [1–4].

Surfactants find specific applications in electroplating, corrosion inhibition, batteries and fuel cells, electro-metallurgy, electro-catalysis, and electro-organic synthesis [5]. Quaternary ammonium based surfactants (QACs) possessing strong attraction for negatively charged surfaces are applied as fabric softeners [6] and disinfectants in medical, food, and beverage industries [7]. It has been documented that positively charged nitrogen groups serve efficiently in antibiotic, antibacterial, and anticancer activities [8, 9]. Many antibiotics are thought to act at the membrane level, but the particular role of nitrogen remains unclear. Mechanistic studies have unraveled that electrostatic attraction with the negatively charged phospholipids can promote a drug's affinity towards a lipid monolayer [10–12].

A literature survey revealed that minimal information exists about electrochemical studies of thiourea-based QACs and no report on the redox behavior of our synthesized compounds *N*-(dodecanoyl(ethylammonio)carbonothioyl)-*N*-ethylbenzenaminium bromide **a** and *N*-(dodecanoyl(ethylammonio)carbonothioyl)-*N*-ethyl-*N*-phenylbenzenaminium bromide **b** is available. Hence spurred on by the unexplored nature of thiourea based cationic surfactants and the broad range of applications, we synthesized and characterized two novel derivatives of this class of surface active agents.

Experimental

Materials and Methods

Analytical grade lauryl chloride, potassium thiocyanate, different aliphatic and aromatic primary and secondary amines

I. Ullah · A. Naveed · A. Shah (✉) · A. Badshah ·
Zia-ur-Rehman · A. Nadeem
Department of Chemistry, Quaid-i-Azam University,
Islamabad 45320, Pakistan
e-mail: afzals_qau@yahoo.com

G. S. Khan
Department of Pharmacy, Quaid-i-Azam University,
Islamabad 45320, Pakistan

and bromoethane were purchased from Sigma-Aldrich and used as received. Fresh analytical grade dry acetone was used as the solvent and dried before experiments. Thin layer chromatography was used for the purification of the product. NMR spectra were recorded on Bruker AC spectrometers at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C. For characterization in the infrared region a thermo Nicolet-6700 FTIR spectrophotometer was used. Electronic absorption spectroscopic experiments were performed on a UV-1800 Shimadzu spectrometer. The pH measurements were done with a WTW inoLab pH 720 meter. Voltammetric experiments were performed using a Digi-Ivy DY2113 Potentiostat, USA. First, 2 mM stock solutions of the synthesized surfactants were prepared in analytical grade ethanol and stored at room temperature. Working solutions of the analyte were prepared in 50 % ethanol and 50 % aqueous supporting electrolytes. Differential pulse voltammetry (DPV) was carried out at a 5 mV s^{-1} scan rate. In the case of square wave voltammetry (SWV), the experimental conditions were a frequency of 20 Hz and 5 mV potential increments to set a scan rate of 100 mV s^{-1}. All the voltammetric experiments were conducted in a highly pure nitrogen atmosphere at room temperature. A glassy carbon electrode (GCE) was used as the working electrode, Pt wire served as a counter electrode and an Ag/AgCl electrode was employed as the reference. The electro active area of the GCE with a value of 0.063 cm^2 was determined as described in the literature [13]. Prior to every experiment the surface of the working electrode was polished with alumina powder followed by thorough rinsing with distilled water.

Synthesis and Purification of the Compounds

*N-(dodecanoyl(ethylammonio)carbonothioyl)-N-ethylbenzenaminium bromide **a***

For the synthesis of compound **a** 0.6 g (0.0063 mol) potassium thiocyanate was dissolved in 50 mL dry acetone and introduced into a 250-mL round-bottom flask after adding 1.5 mL lauryl chloride. Following heating for about 40 min, aniline was added and the solution was kept stirring for 8–10 h. Ethyl bromide was then added and the reaction was kept on reflux for about 4–5 h. The final product was collected by condensing in ice and then it was washed with bi-distilled water. The pure product with 85 % yield was obtained as a white powder. The stepwise

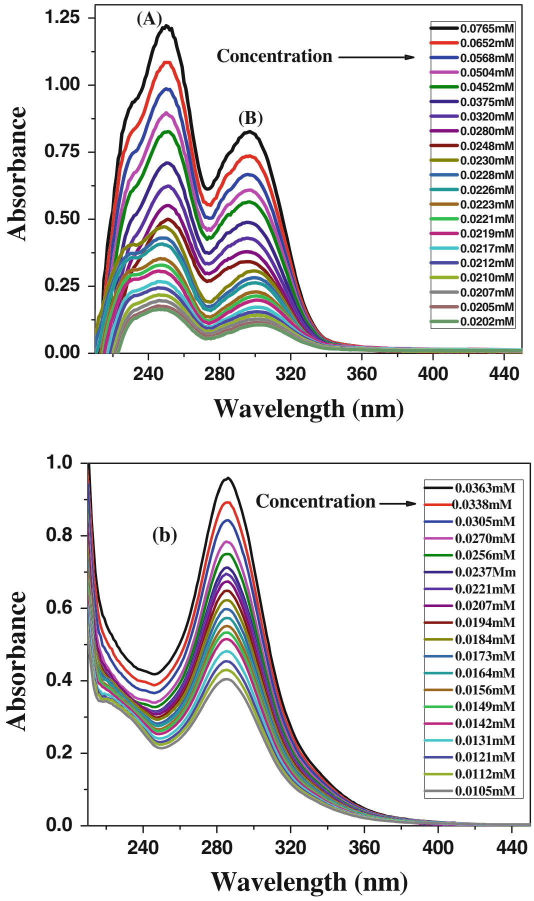
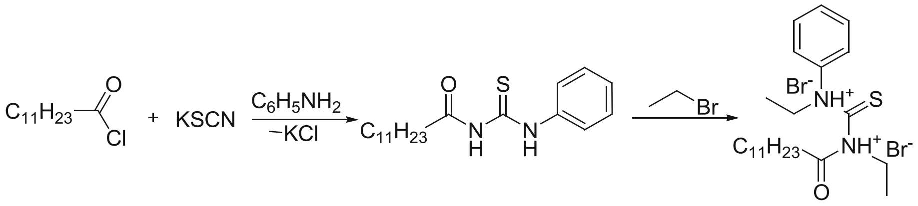
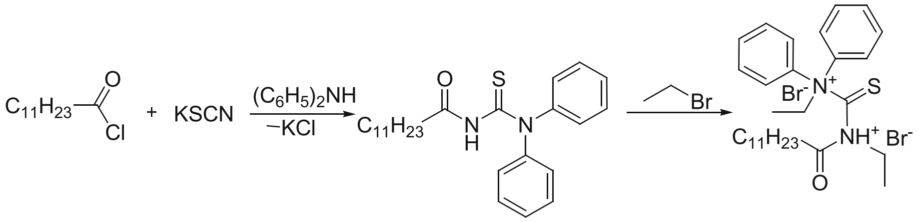


Fig. 1 UV–Vis spectra of compounds **a** and **b**

Scheme 1 Stepwise synthetic description of compound **a**



Scheme 2 Stepwise synthetic description of compound **b**



preparation protocol is given in Scheme 1. The purity of the compound was evidenced by ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy. The spectral details are given below:

^{1}H NMR (300 MHz, $CDCl_3$, δ-ppm): 0.92–0.87 (3H, t, CH_3, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 1.28–1.33 (20H, m, 10CH_2). 1.66–1.73 (6H, t, 2CH_3, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 2.39–2.44 (4H, q, 2CH_2, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 7.27–7.32 (1H, t, H_1, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 7.39–7.45 (2H, t, $H_{2,2}$, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 7.64–77 (2H, d, $H_{3,3}$, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 9.26 (1H, s, $N^{2}H$), 12.46 (1H,s, $N^{1}H$) ^{13}C NMR (75.5 MHz $CDCl_3$, δ-ppm): 14.2 (3CH_3), 22.7–31.9 (10 CH_2), 37.3 ($C_{18,20}$), 124.3 ($C_{3,3}$), 126.9 (C_1), 128.9 ($C_{2,2}$), 137.4 (C_4), 174.7 (C_6), 178.5 (C_5). IR (υ cm^{-1}): 3,387 (N–H), 3,108, 3,031 (Aromatic, C–H, *sp*^{2}), 2,917, 2,848 (*sp*^{3}, C–H), 1,700 (CO), 1,446, 1,596 (*sp*^{2}, C=C).

N-(dodecanoyl(ethylammonio)carbonothioyl)-N-ethyl-N-phenylbenzenaminium bromide **b**

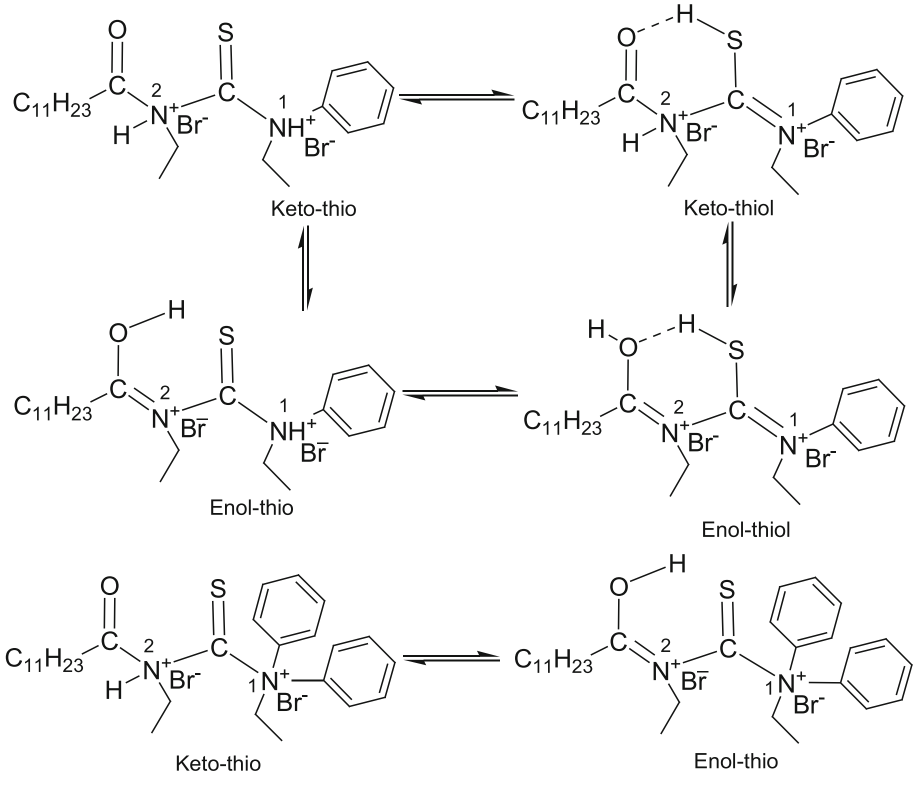
In order to synthesize compound **b**, 0.6 g (0.0063 mol) potassium thiocyanate dissolved in 50 mL dry acetone was transferred into 250-mL round-bottom flask and 1.5 mL lauryl chloride added. After heating for about 40 min diphenylamine was added and the solution kept stirring for 8–10 h. Ethyl bromide was then added and the reaction was kept on reflux for about 4–5 h. Finally the product collected by condensing in ice and cleaned from impurities by washing with doubly distilled water. The pure product with 90 % yield was obtained as a yellow powder. The pattern of synthesis is shown in Scheme 2. The purity of the compound was demonstrated by ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy. The spectral details are given below:

^{1}H NMR (300 MHz, $CDCl_3$, δ-ppm): 0.90–0.95 (3H, t, CH_3, ^{3}J $[^{1}H,^{1}H] = 7$ Hz), 1.23–1.30 (20H, m, 10CH_2). 1.69–1.64 (6H, t, 2CH_3, $^{3}J[^{1}H–^{1}H] = 7$ Hz ($C_{19,21}$)), 2.25–2.40 (4H, q, 2CH_3, $^{3}J[^{1}H–^{1}H] = 7$ Hz), 6.94–6.99 (2H, t, $H_{1,1}$ $^{3}J[^{1}H–^{1}H] = 7$ Hz), 7.13–7.10 (4H, t, $H_{3,3,3,3}$, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 7.28–7.42 (4H, d, $H_{2,2,2,2}$, $^{3}J[^{1}H,^{1}H] = 7$ Hz), 8.72 (1H, s, $N^{2}H$). ^{13}C NMR (75.47 MHz $CDCl_3$, δ-ppm): 14.2 (3CH_3), 22.76–31.96 (10CH_2), 34.1 (C_{20}), 37.0 (C_{18}), 117.7–120.9 ($C_{3,3\ 3,3}$), 127.0–127.5 ($C_{2,2,2,2}$), 129.3 ($C_{1,1}$), 143.1 ($C_{4,4}$), 169.5 (C_6), 182.1 (C_5). IR (υ cm^{-1}): 3,388 (N–H), 3,188, 3,043 (Aromatic, C–H, *sp*^{2}), 2,914, 2,848 (*sp*^{3}, C–H), 1,717 (CO), 1,411, 1,590 (*sp*^{2}, C=C).

Results and Discussion

Structural Characterization

The presence of C=O, C=S, N–H, characteristic stretching vibrations of phenyl ring and *sp*^{3} C–H stretch in the FTIR spectra indicated the formation of surfactants **a** and **b.** In the proton NMR spectrum, a quartet and a triplet for ethyl, a singlet due to CH_3 of the long chain, a singlet due to NH,



Scheme 3 Tautomeric forms of compounds **a** and **b**

CH_2 peaks of the long chain and phenyl resonance with expected multiplicity pattern and integration values confirmed the formation of surfactant **a**. The proton NMR spectrum of **b** was similar to **a** with the exception of N–H and phenyl to have integration values of half and double than that of **a**. Moreover, the presence of expected resonance for carbons in ^{13}C-NMR spectra of structures **a** and **b** further confirmed the successful synthesis of both surfactants.

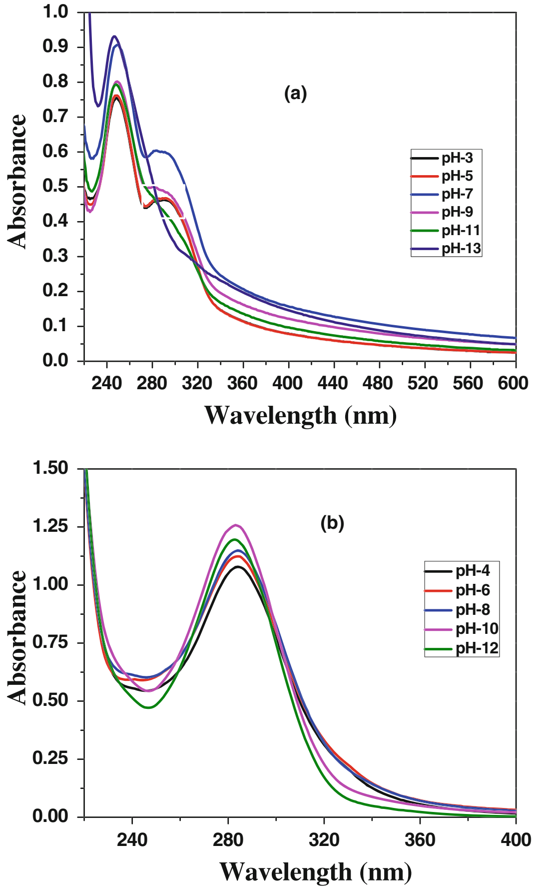
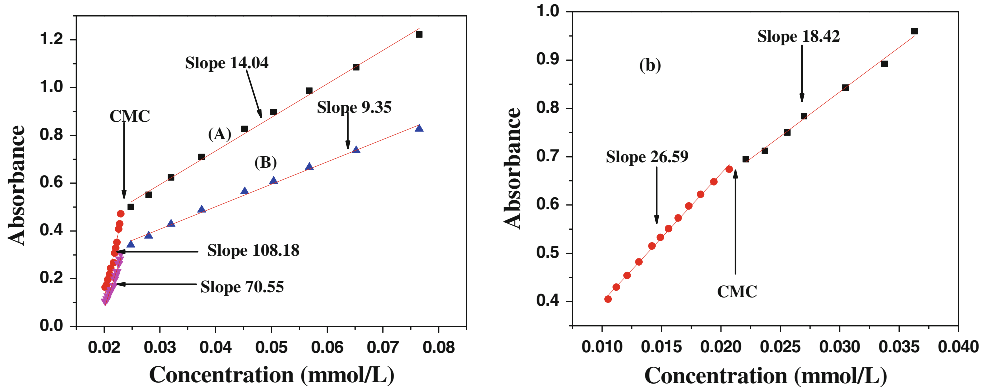


Fig. 2 UV–Vis spectra of compounds **a** and **b** obtained in different pH media

Figure 1 shows the electronic absorption spectra of surfactants **a** and **b**, which exhibited different UV–Visible spectral characteristics. Compound **a** synthesized by the reaction of aniline (primary amine) gave two bands at wavelengths 250 and 302 nm, whereas compound **b** formed by the reaction of diphenylamine (secondary amine) registered a single wave at 285 nm. The peak at 250 nm is attributed to the π–π* transition of the phenyl group. As two phenyl groups are present in the structure of compound **b** so its absorption maxima lies at a longer wavelength (285 nm) with a higher intensity. The second peak of compound **a** at 302 nm is attributable to the π–π* transitions of relatively more conjugated keto-thiol and enol-thiol forms as compared to keto-thio and enol-thio forms (Scheme 3). The absence of a second peak in the UV–Vis spectrum of compound **b** indicates its inability to acquire keto-thiol and enol-thiol tautomeric forms. Reports on tautomerization of surfactants closely related to compounds **a** and **b** are also available in the literature [14–17].

For further clarification of the tautomeric phenomena of compounds **a** and **b**, UV–Visible spectra depicted in Fig. 2 were recorded in different pH media. A clear isosbestic point can be seen in the spectra of compound **a**. No such behavior is observable in the spectra of **b**. Such peculiar spectral characteristic demonstrate that compound **a** exists in tautomeric forms as depicted in Scheme 3 whereas **b** does not show thio-thiol tautomerism. The isosbestic point indicates that the different tautomeric forms of compound **a** absorb the same amount of light at 285 nm. At this wavelength all the tautomeric forms exist as mixtures of constant proportion. At pH 13, compound **a** signaled a single sharp peak due to the possible existence of only the keto-thio form under highly alkaline conditions [18–21]. The CMC of surfactants **a** and **b** with values of 23 and 20 μM were determined from the inflection point of absorbance vs. concentration plots shown in Fig. 3. The quite low CMC values of the synthesized surfactants are

Fig. 3 Absorbance vs. concentration plots of compounds **a** and **b**



comparable with the reported related surfactants [22–26]. The CMC of compound **a** was measured by plotting absorbance of both peaks vs. concentration. The prominent slope difference in the linear segments of the plot of compound **a** as compared to **b** is suggestive of its effective aggregation. The rise in absorption intensity of **a** after the CMC is less sharp than **b** due to the inability of light to approach the inner molecules of comparatively large size micelles. While the steep rise in the absorption of compound **b** after CMC indicates the formation of small sized micelles (having lower aggregation number) in which the inner molecules are not effectively shadowed by the exterior molecules. The steric hindrance due to extra phenyl group is expected to prohibit close packing in **b** and thus cause the formation of micelles with small aggregation number.

Cyclic Voltammetry (CV)

A cyclic voltammogram of 1 mM **a** was recorded in the potential range of −1.3 to +1.25 V at a scan rate of 100 mV s^{-1}. An anodic peak at +0.617 V and a cathodic peak at −0.912 V corresponding to the oxidation and reduction of the analyte were noticed in the forward and backward scans of the same voltammogram. A peak clipping experiment confirmed that the cathodic peak is generated due to the reduction of compound **a**. Cyclic voltammograms obtained at different scan rates (Fig. 4a) revealed that the anodic peak shifts to more positive potential values and the cathodic signal moves in the direction of more negative potentials with an increasing scan rate. The 34 and 107 mV shifts of the anodic and cathodic peaks for a tenfold increase in the scan rate indicated the irreversibility of the redox reactions. Multiple CV scans (Fig. 4b) without cleaning the electrode surface witnessed the shifting of the oxidation peak to more positive potentials accompanied with a diminution of current intensity. Such CV characteristics indicate the deposition of analyte over the electrode surface. Following the same procedure, the cyclic voltammetric behavior of compound **b** was also investigated. The CVs shown in Fig. 4c were obtained at different scan rates in the medium at pH 12. The appearance of anodic and cathodic peaks at lower potentials (+0.407 and −0.762 V) revealed that compound

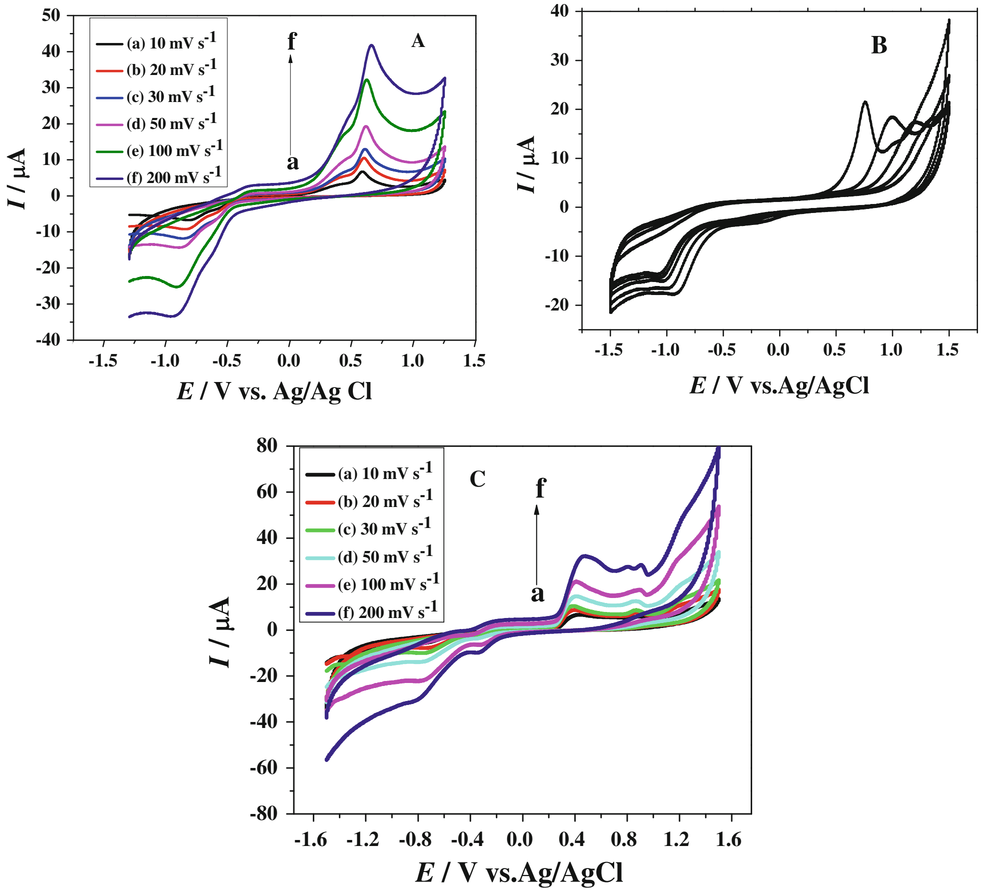


Fig. 4 CVs of 1 mM compound **a** recorded in pH 12 at **A** Different scan rates, **B** Multiple scans at 100 mV s^{-1} and **C** CVs of 1 mM compound **b** recorded in pH 12 at different scan rates

b oxidized and reduced more easily as compared to compound **a**. The electro-oxidation and reduction of **a** and **b** at modest potential values suggest their use as excellent probes for the delivery of drugs [27]. Diffusion coefficients of oxidation ($D_o = 1.32 \times 10^{-4}$ cm^2 s^{-1}) and reduction ($D_R = 7.52 \times 10^{-5}$ cm^2 s^{-1}) of **a** were calculated from the plots of anodic and cathodic currents vs. the square root of the scan rate using the well known Randles–Sevcik equation. The values are well within the range of D reported by previous investigators [28, 29]. The D_o and D_R of compound **b** were determined as 2.70×10^{-5} and 4.53×10^{-5} cm^2 s^{-1} respectively. The slightly smaller D values of compound **b** as compared to **a** is due to its greater molecular mass. Plots of log I_{pa} vs. log ν as shown with slope values between 0.5 and 1.0 indicated that the oxidation process of both compounds are controlled by partial adsorption and partial diffusion [30]. The heterogeneous electron transfer rate constants (k^o) of **a** and **b** based upon the oxidation of bromide ions with values of 1.24×10^{-5} and 2.34×10^{-6} cm s^{-1} were evaluated by using the Reinmuth expression [31]. The values are comparable to Br$^-$ containing compounds reported in the literature [28, 32].

Square Wave Voltammetry

Square wave voltammetry (SWV) is superior to other electrochemical techniques due to a greater speed of analysis, modest consumption of electro active species as compared to DPV and fewer problems with the poisoning of the electrode surface [33]. The main advantage of SWV is that reversibility of the electron transfer process can be checked by a single scan. Since the currents for oxidation and reduction processes are recorded simultaneously in one run, the SWV can reliably demonstrate the reversibility, irreversibility or quasi-reversibility of an electrochemical process.

In order to investigate the redox mechanism, SW voltammograms of compound **a** were obtained in the pH range 3–12. The higher sensitivity of SWV is evident from the observation that the CVs of **a** were able to register only one oxidation peak whereas SWV registered two oxidation peaks. The peak potentials of anodic and cathodic peaks were found to depend strongly on the pH of the medium. The anodic peaks were shifted to more negative potential values in the pH range 3–9 (Fig. 5a) indicating the involvement of protons in the oxidation process and the ease of electron abstraction in alkaline conditions. An unusual change in the trend was observed in highly alkaline media of pH 10–12 when the oxidation peaks were found to shift towards more positive potentials (Fig. 5b). Peak clipping experiment showed that the second anodic signal is independent of peak 1. The structure of **a** has three most feasible oxidation moieties; Br$^-$, S and oxygen with Br$^-$ ions being the easiest to oxidize. Hence, peak 1a is attributed to the oxidation of Br$^-$ attached to N-1 and peak 2a to the oxidation of Br$^-$ bound to N-2, N-1 and N-2 have only one different group in their close vicinity. So the effect of the thio group on both nitrogen atoms is expected to be the same. Due to the electron donating effect of the phenyl group, Br$^-$ will be less tightly bound to N-1 and hence possibly be oxidized at a lower positive potential as compared to Br$^-$ attached to N-2 having an attached electron withdrawing carbonyl group. Figure 5b further demonstrates that in highly alkaline media of pH 11 and 12, peaks 1a and 2a merge into a single intense peak. In strongly alkaline conditions, the quaternary ammonium ions are considered to be surrounded and enveloped by hydroxide ions which will cause both the Br$^-$ ions to become free and hence likely oxidize at the same potential. The reversibility of anodic peaks was examined by SWV at pH 10. The voltammograms presented in Fig. 6a witness the irreversible nature of both peaks. The effect of pH on the potentials of peak 1a and 2a can be seen in Fig. 6b, c. The slope values of 63.9 and 61.6 mV pH^{-1} close to the theoretical value of 59 mV pH^{-1} unit indicate the transfer

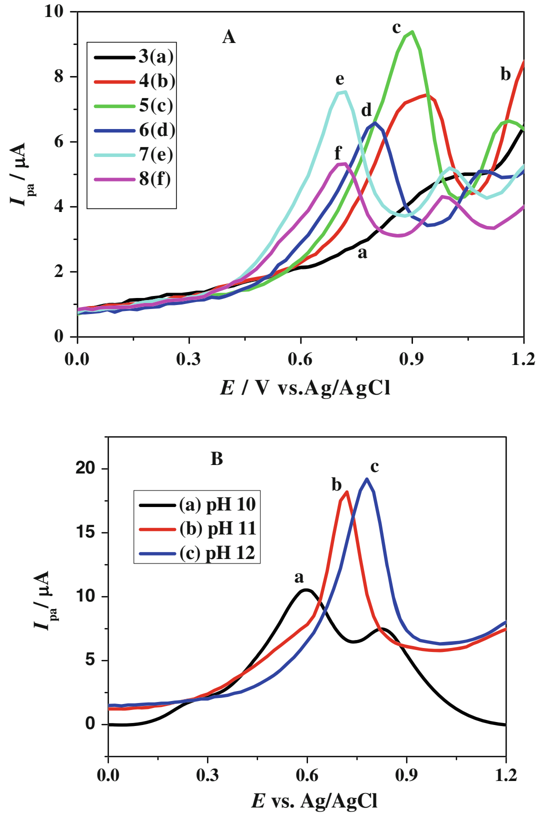


Fig. 5 Square wave voltammogram showing oxidation of compound **a** at 100 mV s^{-1} in pH **A** 3–9 and **B** 10–12

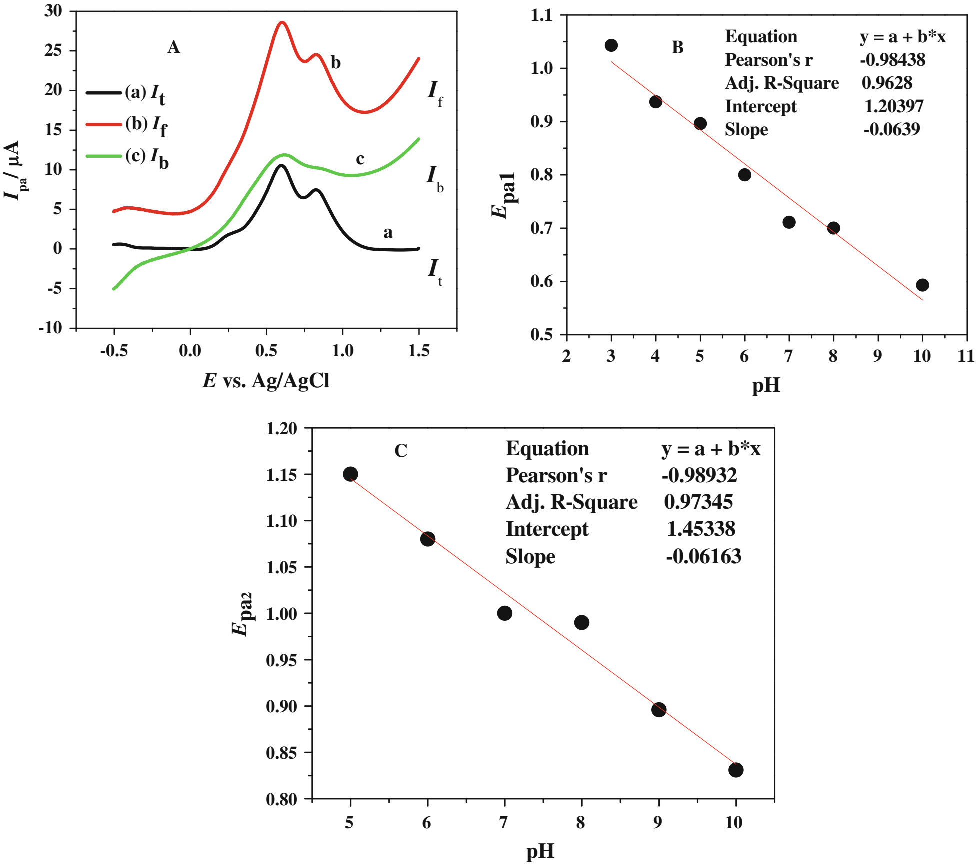
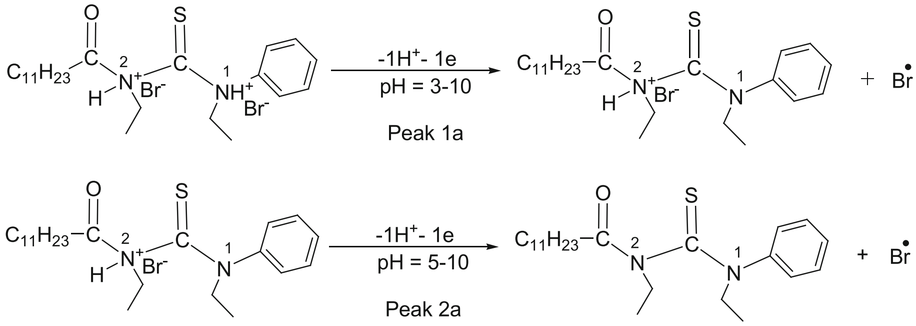


Fig. 6 **A** First scan SW voltammograms of 1 mM compound **a** at 100 mV s^{-1} in pH 10 showing total current (I_t), forward current (I_f) and backward current (I_b), **B** E_{pa} (peak 1) vs. pH, **C** E_{pa} (peak 2) vs. pH



Scheme 4 Proposed electro-oxidation mechanism of compound **a**

of an equal number of electrons and protons. The proposed mechanism is presented in Scheme 4.

In the potential domain of –1.06 to –0.30 V, a single broad cathodic peak shifting in the positive direction was observed in the pH range 3–10 (Fig. 7). Quaternary ammonium ions have positively charged nitrogen atoms which will reduce simultaneously by the gain of one electron and loss of one proton in a narrow potential range, so that the resulting peaks are expected to merge into a single broad peak. At pH 11 and 12 the splitting of the single peak into two validates our attribution of peak broadness and indicates the different reduction potentials of both nitrogen atoms in highly alkaline conditions. The changing of the location of the reduction waves to less negative potentials suggests that reduction becomes easier as the medium becomes more basic.

Differential Pulse Voltammetry (DPV)

DPV is envisioned as reducing background charging currents. The waveform in DPV is a succession of pulses, where a baseline potential is held for a particular period of time earlier than the application of a potential pulse. The current is sampled at time τ just prior to the application of the potential pulse. Differential pulse voltammograms of surfactant **a** recorded in the pH range 3–12 supported the results obtained from SWV. The number of electrons involved in the electro-oxidation of the compound was

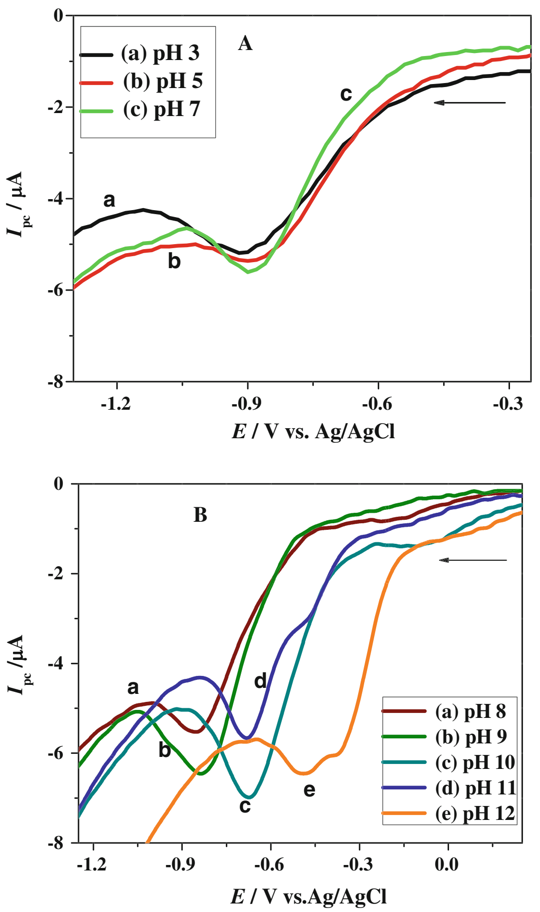


Fig. 7 SW voltammograms showing reduction of compound **a** at **A** pH 3–7, **B** pH 8–12

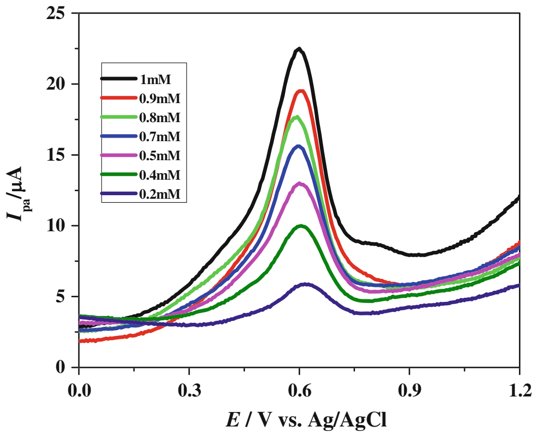


Fig. 8 SW voltammograms showing the oxidation of different concentrations of compound **a** in pH 12 at 100 mV s^{-1}

determined from the DPV shown in Fig. 8. The average peak width ($W_{1/2}$) of 93 mV quite is close to the theoretical value of 90 mV indicating that one electron is involved in the reduction process.

Conclusion

Two cationic surfactants were successfully synthesized in high yield from cheap and easily available starting materials. The synthesized compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR and UV–Vis spectroscopy. The results of UV–Vis spectroscopy demonstrated that *N*-(dodecanoyl(ethylammonio)carbonothioyl)-*N*-ethylbenzenaminium bromide exists in different tautomeric forms with the same molar absorption coefficient at 285 nm as indicated by the isosbestic point. The CMC of both surfactants were evaluated from the inflection point of absorbance vs. concentration plots. Electrochemical results revealed that these surfactants oxidized and reduced independently in a pH-dependent irreversible manner. The detailed electrochemical probing enabled us to propose the redox mechanism and thus predicted the possible fate of this class of surfactants in different pH media. The electro-oxidation and reduction of both surfactants at modest potential values suggested their use as excellent probes for drug delivery.

Acknowledgments The authors gratefully acknowledge the funds provided by Quaid-i-Azam University and the Higher Education Commission, Islamabad, Pakistan, for supporting this work.

References

1. Benedetto D, Shah DO, Kaufman HE (1975) The instilled fluid dynamics and surface chemistry of polymers in preocular tear film. Invest Ophthalm 14:887–902
2. Scramm LL, Stasiuk EN, Marangoni DG (2003) Surfactants and their applications. Annu Rep Prog Chem Sect 99:3–48
3. Rosen MJ (2004) Surfactants and interfacial phenomena, 3rd edn. Wiley, Hoboken, New Jersey
4. Sasikala K, Arunachalam S (2010) Synthesis, characterization, and electron transfer reaction of some surfactant-cobalt (III) complex ions. Monatsh Chem 141:309–316
5. Vittal R, Gomathi H, Kim KJ (2006) Beneficial role of surfactants in electrochemistry and in the modification of electrodes. Adv Colloid Interface Sci 119:55–68
6. Garcia MT, Guinduiain RT, Sanchez-Leas J, Rives-Rego J (2011) Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment. Environ Pollut 111:169–175
7. Boal AK, Rivera S, Sanchez J (2012) Organic contaminant destruction using chlorine or mixed oxidant solution and ultraviolet light, Patent application # 20120298592
8. Kubesch P, Boggs J, Luciano L, Maass G, Tummier B (1987) Interaction of polymyxin B nonapeptide with anionic phospholipids. Biochemistry 26:2139–2149
9. Tritton GR, Yee G (1982) The anticancer agent Adriamycin can be actively cytotoxic without entering cells. Science 217:248–250
10. Goormaghtigh E, Chatelain P, Caspers J, Ruysschaert JM (1981) Lipid-drug electrostatic interactions in model membranes. J Colloid Interface Sci 80:163–170
11. Henry N, Fantine EO, Bolard J, Suillerot AG (1985) Interaction of Adriamycin with negatively charged model membranes: evidence of two types of binding sites. Eur J Biochem 24:7085–7092

12. Burke TG, Sartorelli AC, Tritton TR (1988) Selectivity of the anthracycline for negatively charged model membranes: role of the amino group. Pharmacology 21:274–280
13. Janeiro P, Novak I, Seruga M, Brett AMO (2007) Electroanalytical oxidation of p-coumaric acid. Anal Lett 40:1779–1786
14. Rosen MJ (1978) Surfactant and interfacial phenomena, 1st edn. Wiley, Hoboken, New Jersey
15. Sedaghat T, Jalilian F (2009) New adducts of diorganotin(IV) chlorides with a new multifunctional Schiff base ligand: synthesis and spectral properties. J Iran Chem Soc 6:271–276
16. Iglesias E (2005) Tautomerization of 2-acetylcyclohexanone in assemblies of cationic surfactants. New J Chem 29:457–464
17. Dakiky M, Nemcova I (2000) Aggregation of *O*,*O*′-Dihydroxy azo dyes III. Effect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4″-sulfophenyl)-5-pyrazolone. Dyes Pigments 44: 181–193
18. Gallot S, Thomas O (1993) Fast and easy interpretation of set of absorption spectra: theory and qualitative applications for UV examination of waters and wastewaters. Fresenius J Anal Chem 346:976–983
19. Geissler PL (2005) Temperature dependence of inhomogeneous broadening: on the meaning of isosbestic points. J Am Chem Soc 127:14930–14935
20. Ravichandiran V, Devarajan V, Masilamani K (2011) Determination of ionization constant (P_{ka}) for poorly soluble drugs by using surfactants: a novel approach. Der Pharm Lett 3:183–192
21. Hachemi ZE, Mancini G, Ribo JM, Sorrenti A (2008) Role of the hydrophobic effect in the transfer of chirality from molecules to complex systems: from chiral surfactants to porphyrin/surfactant aggregates. J Am Chem Soc 130:15176–15184
22. Dufour M, Guyot A (2003) Nonionic reactive surfactants. I. Synthesis and characterization. Colloid Polym Sci 281:97–104
23. Negm NA, Aiad IA (2007) Synthesis and characterization of multifunctional surfactants in oil-field protection applications. J Surf Deterg 10:87–92
24. Anounea N, Nouirib M, Arnauda C (2000) Prediction of critical micelle concentration of some anionic surfactants using multiple regression techniques: a quantitative structure-activity relationship study. J Surf Deterg 3:381–386
25. Tahirat N, Luis A, Mindy L (2011) Determination of critical micelle concentrations using UV–Visible spectroscopy. J High Sch Re 2:1–6
26. Mata J, Varade D, Bahadur P (2005) Aggregation behavior of quaternary salt based cationic surfactants. Thermochim Acta 428:147–155
27. Kovacic B, Vrecer F, Planinsek O (2011) Design of a drug delivery system with bimodal pH dependent release of a poorly soluble drug. Pharmazie 66:465–466
28. Allen GD, Buzzeo MC, Villagra C, Hardacre C, Compton RG (2005) A mechanistic study of the electro-oxidation of bromide in acetonitrile and the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at platinum electrodes. J Electroanal Chem 575:311–320
29. Park KH, Jin EM, Park BK, Gu HB (2009) Electrochemical properties of dye-sensitized plasma treated nano-structured TiO films. ECS 2:748
30. Nosheen E, Shah A, Badshah A, Rehman Z, Hussain H, Qureshi R, Ali S, Siddiq M, Khan AM (2012) Electrochemical oxidation of hydantoins at glassy carbon electrode. Electrochim Acta 80:108–117
31. Nadjo L, Savéant JM (1973) Linear sweep voltammetry: kinetic control by charge transfer and/or secondary chemical reactions: I formal kinetics. J Electroanal Chem 48:113–145
32. Shin CB, Economou DJ (1991) Force and natural convection effects on the shape evolution of cavities during wet chemical etching. J Electrochem Soc 138:527–538
33. Gole DA, Diculescu VC, Enache AT, Butu A, Tugulea L, Brett AMO (2012) Electrochemical evaluation of dsDNA-liposomes interactions. Dig J Nanomater Bios 7:1333–1342

Author Biographies

Imdad Ullah is an assistant professor in the government college of Khyber Pakhtunkhwa, Pakistan. Currently he is a Ph.D. graduate student in the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan. He has synthesized more than twenty new thiourea-based surfactants.

Ahmad Naveed was awarded his M.Sc. degree by the Quaid-i-Azam University (QAU) Islamabad in 2011. He completed his M.Phil. from QAU under the supervision of Dr. Afzal Shah. His research is focused on the electrochemical fate of surfactants in different pH media.

Afzal Shah received his Ph.D. in physical chemistry from Quaid-i-Azam University in 2010 under the indigenous Ph.D. program launched by the Higher Education Commission of Pakistan. He has worked in surfactant chemistry and electrochemistry.

Amin Badshah is a professor in chemistry at Quaid-i-Azam University, Ismalabad, Pakistan. He has focused on the synthesis, characterization and applications of surfactants and medicinal compounds. He has been included in the list of "Leading Scientists and Engineers of OIC Member States", published by COMSTECH Secretariat, Islamabad, Pakistan.

Zia-ur-Rehman earned his Ph.D from the Department of Chemistry, Quaid-i-Azam University, Islamabad in 2009 under the HEC indigenous program. Through a HEC IRSEP scholarship he studied in McGill University, Canada. Presently, he is assistant professor in the Department of Chemistry, Quaid-i-Azam University, Islamabad. His research interests include discovery of new metal-based anticancer drugs and their targeted delivery via loading in micelles of body compatible surfactants.

Gul Shahzada Khan earned his M.Sc. and M.Phil. degrees from the Department of Chemistry, Quaid-i-Azam University (QAU), Islamabad, Pakistan. He did his graduate research work in the School of Chemical Sciences, University of Auckland, New Zealand and received his Ph.D. in 2011. Then, he joined the Department of Pharmacy, QAU as an assistant professor of organic chemistry. His research interests include development of new synthetic routes to prepare surfactants and complex molecules with interesting biological activities, reaction mechanism of organic molecules and isolation, characterization and biological activities of secondary metabolites from plants.

Arif Nadeem received his Ph.D. from the University of New South Wales, Sydney in 2011. Then, he joined the Department of Chemistry, QAU as an assistant professor of inorganic chemistry. His research interests include metal–organic frameworks, nanotechnology, surfactant synthesis and catalysis.