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Self-Aggregation and Liquid Crystalline Behavior of New Ester-Functionalized Quinuclidinolium Surfactants

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Supporting Information

ABSTRACT: A new type of ester-based cationic surfactant having a quinuclidinolium headgroup has been synthesized starting from linear fatty alcohols and has been characterized using spectroscopic techniques. The self-aggregation and thermodynamic properties of these surfactants have been investigated by pendant-drop surface tensiometry and conductivity measurements. The liquid crystalline behaviors of these surfactants were investigated by small-angle X-ray scattering (SAXS) technique. The quinuclidinolium headgroup demonstrated a unique ability to interlock among themselves thus



affecting the physicochemical properties of surfactants in aqueous solution. The current research finding supports the new concept of headgroup interlocking which is supported by 1D and 2D NMR studies.

1. INTRODUCTION

Cationic surfactants are an important category of amphiphilic molecules which are an important constituent of several industrial formulations and consumer products. The most common headgroup being used in many technical applications is the quaternary ammonium group, among the other heterocyclic cationic surfactants.^{1,2} The surface active portion or the hydrophilic group of these surfactants bears a positive charge, and they dissociate in water as an amphiphilic cation and an anion. Since this category of surfactants consists of acyclic or heterocyclic positively charged quaternary ammonium headgroups, they are able to adsorb on most of the negatively charged surfaces.³ Because of this predominant character, these surfactants have been used in many technical and nontechnical areas as fabric softeners, electrodip coatings, and in the stabilization of adhesive polymer latexes as well as in mining and paper manufacturing. In recent years the environmental concerns have shifted the focus of the surfactant chemist toward developing and investigating biocompatible cationic surfactants having significant portion of functional groups that can be easily degraded in the environment after use. Most recently several ester-functionalized heterocyclic, i.e., pyridinium,⁴ imidazolium, piperidinium,⁵ and pyrrolidinium,⁶ surfactants have demonstrated superior physicochemical properties compared to conventional monomeric cationic surfactants. Ester functional group is considered biocompatible and is easily degraded in the environment, and their quaternary ammonium derivatives have been found to be hydrolyzable.^{7,}

In the present work new ester-functionalized quinuclidinolium surfactants have been synthesized starting from linear fatty alcohols (Scheme 1). These new surfactants consist of quinuclidinolium moiety as a hydrophilic headgroup and linear fatty alcohol ester as a hydrophobic tail. Quinuclidine moiety exists in several plant-based natural products as an alkaloid and is naturally found in many *Cinchona* species. Synthetic derivatives of quinuclidine have medicinal properties^{9,10} and are commonly used as catalysts for organic reactions.¹¹ Several reports are available regarding heterocyclic cationics containing pyridinium,^{12,13} imidazolium,¹⁴ pyrrolidinium,¹⁵ and piperidinium¹⁶ as a hydrophilic headgroup; however, more complicated and bulky headgroups like quinuclidinolium have never been investigated for their self-aggregation and physicochemical properties.

We expect that the unique molecular design of quinuclidinolium headgroups enables them to interlock among themselves thus greatly effecting the physicochemical properties of the surfactants in water. The surface and thermodynamic parameters of the new ester-functionalized quinuclidinolium surfactants such as surface excess concentration (Γ_{cmc}), surface area occupied by molecule at the air/water interface (A_{\min}) , efficiency in surface tension reduction by 20 mN/m (C_{20}), the effectiveness of surface tension reduction (γ_{min}), critical micelle concentration (cmc), degree of counterion binding (β), and standard free energy of micellization $(-G^0_{\rm mic})$ and adsorption $(-G^{0}_{ads})$ have been evaluated by surface tension measurements and conductivity method. The lattice parameter (α') for liquid crystalline phases of the quinuclidinolium surfactant-water system and other important parameters, i.e., the radius of the cylinder units $(d_{\rm H})$, cross-sectional area per surfactant at the interface (a_s) , and the distance between the cylinders (d_w) , have been determined by SAXS experiments.

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Scheme 1



2. MATERIAL AND METHODS

2.1. Materials. Lauryl alcohol, myristyl alcohol, chloroacetic acid, *p*-toluenesulfonic acid monohydrate, and 3-quinuclidinol were purchased from TCI, Tokyo, Japan. The alkyl-2-chloroacetates were prepared according to the modified procedure of a previously reported literature report.⁶

2.2. Synthesis. Lauryl alcohol (1; 9.32 g, 50 mmol) or myristyl alcohol (2; 10.72 g, 50 mmol) were reacted with chloroacetic acid (3; 5.20 g, 55 mmol) in the presence of a catalytic amount of p-toluene sulfonic acid monohydrate (4; 951 mg, 5 mmol) under solvent-free conditions for 4 h at 80 °C. The reaction mixture was then allowed to cool at room temperature and then was dissolved in 100 mL of chloroform and washed twice with 100 mL of water. The chloroform layer was separated with a separating funnel and was removed from the crude reaction mixture under reduced pressure in a rotary flash evaporator at 40 °C. The crude reaction mixture was then washed with 100 mL of warm aqueous methanol (92:8, methanol:water). The lower layer consisting of alkyl 2-chloroacetates (5-6) was allowed to separate in the separating funnel. It was then separated, dissolved in hexane, dried using Na2SO4, and filtered. The solvent was removed in vacuum rotary flash evaporator at 80 °C for 30 min. The resulting intermediates alkyl 2-chloroacetate, i.e., dodecyl 2-chloroacetate (5; 6.57 g, 25 mmol) or tetradecyl 2-chloroacetate (6; 7.27 g, 25 mmol), were then reacted with 3-quinuclidinol (7; 3.18 g, 25 mmol) at 50 °C for 4 h in 20 mL of CHCl₃ (Scheme 1). The chloroform was removed by rotary evaporator at 60 °C. The resulting crude mixture was cooled to 25 °C. The product was washed thrice with 100 mL of diethyl ether and then cold precipitated in 100 mL of acetone to get new esterfunctionalized quinuclidinolium surfactants 12QuinucEsCl (8) and 14QuinucEsCl (9). The structures of these surfactants were confirmed by NMR and high-resolution mass spectroscopy (HRMS). Mass spectra of surfactants were recorded on a JEOL JMS-T100CS (JEOL Japan) using ESI as ion source. ¹H, ¹³C NMR, 2D COSY, and 2D NOESY spectra were recorded on a JEOL-ECP500 (JEOL Japan) as a solution in D₂O.

1-(2-(Dodecyloxy)-2-oxoethyl)-3-hydroxyquinuclidin-1-ium chloride (8). White solid, yield 83%; 500 MHz ¹H NMR (D₂O) δ ppm: 0.88 (m, 3H), 1.26 (br s, 18H), 1.70 (m, 2H), 2.00 (m, 2H), 2.16 (m, 1H), 2.31 (m, 1H), 2.35 (m, 1H), 3.59 (m, 2H), 3.70 (m, 2H), 3.78 (m, 1H), 3.95 (m, 1H), 4.22 (br s, 2H), 4.35 (br s, 3H). ¹³C NMR (D₂O) δ ppm: 12.70, 16.27, 19.79, 21.56, 24.56, 27.02, 28.37, 28.53, 28.88, 28.95, 29.05, 30.94, 54.21, 54.45, 60.17, 61.95, 62.91, 65.17, 163.85. ESI-HRMS positive ions *m*/*z*: calculated 354.3003 for C₂₁H₄₀NO₃⁺ (M–Cl or M⁺), found 354.3004.

1-(2-(Tetradecyloxy)-2-oxoethyl)-3-hydroxyquinuclidin-1-ium chloride (**9**). White solid, yield 84%; 500 MHz ¹H NMR (D₂O) δ ppm: 0.88 (m, 3H), 1.30 (br s, 22H), 1.70 (br s, 2H), 1.99 (br s, 2H), 2.30 (m, 1H), 2.35 (m, 1H), 2.30 (m, 1H), 3.59 (m, 2H), 3.70 (m, 2H), 3.79 (m, 1H), 3.95 (m, 1H). ¹³C NMR (D₂O) δ ppm: 12.73, 16.28, 19.82, 21.57, 24.55, 27.03, 28.32, 28.50, 28.77, 28.83, 30.93, 54.28, 54.49, 60.23, 61.98, 62.95, 65.28, 163.87. ESI-HRMS positive ions m/z: calculated 382.3316 for C₂₃H₄₄NO₃⁺ (M–Cl or M⁺), found 382.3317.

2.3. Surface Tension Measurements Using Pendent Drop Tensiometer. The surface tension at the water-air interface was investigated using the pendant drop technique^{17,18} (Kyowa Drop Master 700, Tokyo, Japan) at 25 °C. An inverted 16-gauge needle is submerged in the aqueous phase such that the tip is visible in the frame of capture. A gas-tight syringe is mounted in a microsyringe pump to ensure instantaneous creation of a droplet of a preset volume. Before the droplet is formed, the image capture software is triggered, collecting images at 20 frames for the first 10 min and 1 frame/min thereafter, for a total aging time of 3600 s (1 h). Edge detection is used to identify the droplet shape, with the surface tension determined using the Young–Laplace equation. Experimental runs of 3600 s are chosen as surfactant solution attains equilibrium within the chosen time frame.

2.4. Conductivity Measurements. Conductivity was measured on auto-temperature electrical conductivity meter CM-25R (DKK-TOA Corporation) equipped with a conductivity cell having a cell constant of 1. The solutions were thermostated at 25.0 ± 0.1 , 30.0 ± 0.1 , 35.0 ± 0.1 , and 40.0 ± 0.1 °C in a thermostated glass vessel controlled by temperature controller. For the determination of cmc, an adequate quantity of a concentrated surfactant solution was added to water in order to change the surfactant concentration from concentrations well below the critical micelle concentration (cmc) to up to at least 2–3 times the cmc. Degree of counterion binding (β) has been calculated as $(1 - \alpha)$, where $\alpha = S_{\text{micellar}}/S_{\text{premicellar}}$ i.e., ratio of the slope after and before cmc.

2.5. Sample Preparation and SAXS Measurements. Samples were prepared in screw-capped glass tubes by weighing appropriate surfactant and water. The tubes were sealed and kept at 80 °C for 1 h, then vortexed for 10 min, and centrifuged at 3500 rpm for 30 min. The procedure was repeated thrice, and the samples were kept for 1 week to attain equilibrium. Measurements were performed using a SAXSess camera (Anton Paar, PANalytical) attached to a PW3830 laboratory Xray generator with a long fine focus sealed glass X-ray tube (KR wavelength of 0.154 nm; PANalytical). The apparatus was operated at 40 kV and 50 mA. The SAXSess camera is equipped with focusing multilayer optics and a block collimator for an intense and monochromatic primary beam with low background, and a translucent beam stop for the measurement of an attenuated primary beam at zero scattering vector (q = 0). Samples were enclosed in a vacuum-tight thin quartz capillary with an outer diameter of 1 mm and thickness of 10 μ m. Sample temperature was controlled with a thermostated sample holder unit (TCS 120, Anton Paar). The 2D scattering pattern was collected on an image plate (IP) detection system Cyclone (PerkinElmer) and was finally integrated into one-dimensional scattering curves as a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ using SAXSQuant software (Anton Paar), where θ is the total scattering angle and λ is the wavelength of the Xray. All data were normalized to the same incident primary beam intensity for the transmission calibration and were corrected for background scattering from the capillary and the solvent.^{19,20}

3.0. RESULTS AND DISCUSSION

3.1. Molecular Characterization. Linear fatty alcohols (lauryl alcohol and myristyl alcohol) were reacted with chloroacetic acid in the presence of a catalytic amount of *p*-toluene sulfonic acid monohydrate under solvent-free conditions to get alkyl-2-chloroacetate, which was then reacted

with 3-quinuclidinol to get ester-functionalized quinuclidinolium surfactants. The structures of these new quinuclidinolium surfactants have been established by ¹H, ¹³C NMR, and highresolution mass spectroscopy (HRMS). The resonance for the methylene protons directly attached to the heterocyclic positively charged quinuclidinolium nitrogen and -CHproton of the quinuclidinolium ring attached to the hydroxyl group were observed at δ 4.35 and 4.37 ppm as broad singlet for 12QuinucEsCl and 14QuinucEsCl, respectively. The chemical shifts for six methylene protons of the quinuclidinolium ring adjacent to the positively charged nitrogen are diastereotopic in nature and were observed overlapping between δ 3.59 and 3.95 ppm integrating for total six protons. The other four methylene protons attached to the β carbon of the quinuclidinolium ring are also diastereotopic in nature and were observed along with the -CH- proton attached to the γ carbon of the quinuclidinolium ring between δ 1.99 and 2.35 ppm. The signal for this proton adjacent to ester functionality in the hydrophobic alkyl chain was observed at δ 4.21 ppm.

The structures of these quinuclidinolium surfactants have been further established by high-resolution mass spectroscopy (ESI-HRMS positive ion). The parent ion peak for the surfactants has been observed for positive ion minus chloride ion from each surfactant molecule. The calculated m/z values (354.3003 for 12QuinucEsCl and 382.3316 for 14QuinucEsCl) closely matched the observed values (354.3004 for 12QuinucEsCl and 382.3317 for 14QuinucEsCl) establishing high purity of the synthesized surfactant molecules.

3.2. Dilute Aqueous Solution Properties. Figure 1 shows the surface tension plot of the quinuclidinolium



Figure 1. Surface tension vs log C plot for the quinuclidinolium surfactants.

surfactants. The surface parameters of these surfactants are given in Table 1. The cmc values of ester-functionalized quinuclidinolium surfactants decrease with the increase in hydrophobic alkyl chain length. The cmc values of 12QuinucEsCl and 14QuinucEsCl have been found to be 5.11 and 1.41 mM, respectively which is almost four times less compared to the commercially available quaternary ammonium surfactants: dodecyltrimethylammonium chloride and tetradecyltrimethylammonium chloride.²¹ The cmc values of these surfactants have also been found to be less compared with the heterocyclic pyridinium and imidazolium surfactants: 1alkylpyridin-1-ium chloride and 1-methyl-3-alkyl-1*H*-imidazol-3-ium chloride having similar hydrophobic alkyl chain length.^{22–25}

The maximum surface excess concentration at the air/water interface, Γ_{max} , is calculated by applying the Gibbs adsorption isotherm equation:

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d\log C} \right)_T$$
(1)

Here, γ denotes the surface tension, *R* is the gas constant, *T* is the absolute temperature, and *C* is the surfactant concentration.⁶ The value of *n* is taken as 2. The area occupied per surfactant molecule (A_{\min}) at the air water interface is obtained by using the following equation:

$$A_{\min} = 1/N\Gamma_{\max} \tag{2}$$

where N is Avogadro's number and A_{\min} is in nm². The values of Γ_{\max} and A_{\min} are shown in Table 1. The A_{\min} values of quinuclidinolium surfactants have been found to be exceptionally low. Both 12QuinucEsCl and 14QuinucEsCl form tighter packing at the air-water interface.

The quinuclidinolium headgroup is bulky and structurally different compared to other types of heterocyclic cationic headgroups. Both hydrophobic alkyl chain and hydrophilic headgroups influence the self-aggregation behavior of the surfactant molecule in water and the molecular arrangement of surfactant monomers at the air—water interface. However, the role of different types of cationic headgroup is seldom investigated. We have found that quinuclidinolium headgroup dramatically influences the aggregation behavior at both low and high concentrations. To understand the forces regulating the self-aggregation behavior of the new quinuclidinolium surfactants, we have to compare quinuclidinolium headgroup with other categories of heterocyclic cationic headgroups (Figure 2).

The pyridinium cation can be described as an aromatic ring system where the positive charge is delocalized throughout the ring and not centric to positively charged quaternary nitrogen. This is supported by the fact that all the pyridinium protons are highly deshielded and often observed downfield in ¹H NMR spectra.²⁶ The delocalized positive charge is counterbalanced by an oppositely charged couterion; however, the intramolecular distance between two headgroups is also regulated by repulsive forces operating between the two positively charged pyridinium headgroups²⁷ although the hydrophobic interaction plays a dominant role in such arrangement. On the contrary, the imidazolium headgroup is totally different compared to others as the -NCHN- proton of imidazolium cation is strongly deshielded and acidic in nature since imidazolium cation forms C==N π bond, leaving the carbon in the center between two

Table 1. Surface Properties of 12QuinucEsCl and 14QuinucEsCl at 25 °C

surfactant	cmc^{a} (mM)	cmc^{b} (mM)	$\gamma_{cmc}~(mN/m)$	$10^6 \ \Gamma_{max} \ (mol/m^2)$	$A_{\min} (\mathrm{nm}^2)$	C_{20} (M)
12QuinucEsCl	5.11 (±0.01)	5.33 (±0.01)	28.9 (±0.1)	3.01 (±0.02)	$0.55 (\pm 0.02)$	9.12×10^{-4}
14QuinucEsCl	1.41 (±0.01)	1.45 (±0.01)	38.0 (±0.1)	3.16 (±0.02)	$0.53 (\pm 0.02)$	5.62×10^{-4}

^acmc determined by surface tension method. ^bcmc determined by conductivity method.



Quinuclidinolium cation observed from different axial angle

Figure 2. Energy-minimized structures of different positively charged heterocyclic positively charged cations. The energy minimization was performed with ChemBio3D Ultra 13.0 software (ChemOffice, CambridgeSoft Corp.) using MM2 molecular mechanics.

nitrogens with concentrated positive charge.²⁸ The sphere of positive charge keeps the adjacent imidazolium moiety at a certain distance; however, again the dominating force is regulated by hydrophobic interaction. The nonaromatic heterocyclic headgroup, i.e., pyrrolidinium and piperidinium, arranges itself in such a way that the essence of carbon-carbon single bond angle is maintained although the conformation in the case of piperidinium cation may be influenced by charge to some extent.²⁹ Quinuclidinolium headgroup is completely different from the previously discussed heterocyclic headgroups. The structural design of this bulky headgroup creates molecular cavities between the extended carbon arms of this moiety (Figure 2), and the presence of additional hydroxyl group enhances the hydrophilic nature of the headgroup. The carbon arm of adjacent quinuclidinolium moiety arranges very closely into the cavity formed by similar moiety, and this is responsible for lower Amin values of these surfactants and compact packing at the interface.

The cmc values of 12QuinucEsCl and 14QuinucEsCl surfactants have further been evaluated by conductivity method at vairous temperatures. The experimental conductivity has been plotted as a function of surfactant concentration at various temperatures (Figure 3).

The cmc values of quinuclidinolium surfactants increase with increase in temperatures. The cmc value follows the same trend as previously investigated by surface tension measurements. The degree of counterion binding (β) for the surfactants has been calculated from the slopes of two linear regimes. Initially

the ratio of the slopes in two regions gives a degree of counterion dissociation (α). The β value has been calculated from the following relationship: $\beta = 1 - \alpha$. The β values of these surfactants slightly decrease with increase in temperature of the surfactant solutions; however, change in length of hydrophobic alkyl chain does not significantly affect this value. This anomalous behavior is in contrast with the trend observed for the previously reported β values of ester-functionalized heterocyclic surfactants.^{4,6}

The thermodynamics of these surfactants according to pseudophase model of micellization⁶ and Gibbs free energy for micellization ($\Delta G^{\circ}_{\rm mic}$) have been calculated from the following equation

$$\Delta G^{\circ}_{\rm mic} = RT(2 - \beta) \ln X_{\rm cmc} \tag{3}$$

where $X_{\rm cmc}$ is the cmc in molar fraction, $X_{\rm cmc} = {\rm cmc}/{\rm 55.4}$, where cmc is in mol/L, and 55.4 comes from 1 L of water corresponding to 55.4 mol of water at 25 °C. Similarly the Gibbs free energy of adsorption ($\Delta G^{\circ}_{\rm ads}$) is calculated by following equation:

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - \frac{\pi_{cmc}}{\Gamma}$$
(4)

Here, $\pi_{\rm cmc}$ denotes the surface pressure at the cmc ($\pi_{\rm cmc} = \gamma_{\rm o} - \gamma_{\rm cmc}$, where $\gamma_{\rm o}$ and $\gamma_{\rm cmc}$ are the surface tensions of water and the surfactant solution at cmc, respectively). The standard enthalpy change for micellization process ($\Delta H^{\circ}_{\rm mic}$) can be determined using the Gibbs–Helmholtz equation:

$$\Delta H^{\circ}_{\rm mic} = \left(\frac{\partial (\Delta G^{\circ}_{\rm mic}/T)}{\partial (1/T)}\right) \tag{5}$$

$$\Delta H^{\circ}_{\rm mic} = -RT^2 (2 - \beta) \ln X_{\rm cmc} / dt \tag{6}$$

The standard entropy of micelle formation (ΔS°_{mic}) can be calculated according to the following equation:

$$\Delta S^{\circ}_{\rm mic} = (\Delta H^{\circ}_{\rm mic} - \Delta G^{\circ}_{\rm mic})/T \tag{7}$$

The thermodynamic parameters, i.e., $\Delta G^{\circ}_{\text{mic}}$, $\Delta H^{\circ}_{\text{mic}}$, and $\Delta S^{\circ}_{\text{mic}}$ of ester-functionalized quinuclidinolium surfactants at different temperatures are shown in Table 2.

It has been observed that the ΔG°_{mic} values for the quinuclidinolium surfactants under investigation are negative and generally decrease with increase in temperature which manifests that the formation of micelle is a spontaneous



Figure 3. Specific conductivity (κ) versus the concentration of (a) 12QuinucEsCl and (b) 14QuinucEsCl at different temperatures.

Table 2. Surface and Thermodynamic Parameters of Quinuclidinolium Surfactants Determined by the Electrical Conductivity Method at Different Temperatures

	T	cmc	β	$\Delta G^\circ_{ m mic}$	$\Delta G^\circ_{ m ads}$	$\Delta {H^{\circ}}_{ m mic}$	$-T\Delta S^{\circ}_{\rm mic}$	$\Delta S^{\circ}{}_{ m mic}$
surfactant	(°C)	$(mmol \cdot L^{-1})$	(%)	$(kJ mol^{-1})$	$(kJ mol^{-1})$	$(kJ mol^{-1})$	$(kJ mol^{-1})$	$(J mol^{-1} \cdot K^{-1})$
12Quinuc EsCl	25 ± 0.1	5.33 (±0.01)	57.2 (±0.1)	$-32.74 (\pm 0.05)$	$-47.06(\pm 0.05)$	$-2.83 (\pm 0.05)$	$-29.91 (\pm 0.05)$	100.31 (±0.1)
	30 ± 0.1	5.41 (±0.01)	56.3 (±0.1)	$-33.44 (\pm 0.05)$		$-2.95 (\pm 0.05)$	$-30.50 (\pm 0.05)$	100.60 (±0.1)
	35 ± 0.1	5.48 (±0.01)	55.3 (±0.1)	$-34.19 (\pm 0.05)$		$-3.07 (\pm 0.05)$	$-31.12 (\pm 0.05)$	100.99 (±0.1)
	$40~\pm~0.1$	5.55 (±0.01)	54.8 (±0.1)	$-34.81 (\pm 0.05)$		$-3.18 (\pm 0.05)$	$-31.63 (\pm 0.05)$	101.02 (±0.1)
14Quinuc EsCl	25 ± 0.1	1.45 (±0.01)	57.1 (±0.1)	$-37.37 (\pm 0.05)$	$-48.13 (\pm 0.05)$	-6.93 (±0.05)	$-30.44 (\pm 0.05)$	102.11 (±0.1)
	30 ± 0.1	1.50 (±0.01)	56.0 (±0.1)	$-38.17 (\pm 0.05)$		$-7.22 (\pm 0.05)$	$-30.95 (\pm 0.05)$	102.09 (±0.1)
	35 ± 0.1	1.55 (±0.01)	54.6 (±0.1)	$-39.05 (\pm 0.05)$		-7.53 (±0.05)	$-31.52 (\pm 0.05)$	102.29 (±0.1)
	40 ± 0.1	1.60 (±0.01)	53.8 (±0.1)	-39.79 (±0.05)		$-7.81 (\pm 0.05)$	$-31.96(\pm 0.05)$	102.07 (±0.1)
	2.5				2.5			



Figure 4. SAXS pattern for the hexagonal phases for (a) 12QuinucEsCl:water and (b) 14QuinucEsCl:water systems at different weight percents at 25 °C.

process. The values for $\Delta H^{\circ}_{\rm mic}$ are negative indicating that the micelle formation is an exothermic process and decreases with the increase in temperature for each individual surfactant under investigation. The absolute values of both $\Delta G^{\circ}_{\rm mic}$ and $\Delta H^{\circ}_{\rm mic}$ increase with the increase in hydrophobic alkyl chain for the quinuclidinolium surfactants. The entropy change ($\Delta S^{\circ}_{\rm mic}$) with increasing temperature as well as increase in hydrophobic alkyl chain has little effect on the micellization process. This anomalous behavior can be explained on the basis of interlocking of the quinuclidinolium headgroup which invalidates the effect of transfer of hydrocarbon chains from water into the interior of micelle.

3.3. Characterization of LC. The quinuclidinolium surfactants (12QuinucEsCl and 14QuinucEsCl) were investigated up to 66 and 57 wt % respectively in water. Above these concentrations, the phases were not found to be stable, and reproducibility does not offer consistent results. Below 48 wt % (in the case of 12QuinucEsCl) and 44 wt % (in the case of 14QuinucEsCl), these surfactants exist as a micellar solution. 12QuinucEsCl forms a hexagonal H1 LC phase at 49-66 wt % while 14QuinucEsCl forms a similar phase at 45-57 wt % in water at 25 °C. The SAXS data give information about the LC phase arranged in a particular fashion. The Bragg reflections corresponding to particular arrangement demonstrated the existence of hexagonal packing. Figure 4 shows the SAXS patterns for the representative samples of H1 phase of 12QuinucEsCl-H₂O and 14QuinucEsCl-H₂O systems at 25 °C. The value of scattering vector q was found to be in the ratio $q1:q2:q3 = 1:\sqrt{3:2}$ for both 12QuinucEsCl and 14QuinucEsCl

suggesting the existence of cylindrical self-assembly crystals in a hexagonal lattice.

The lattice parameter α' is calculated from the first peak position by $\alpha = (4\pi/\sqrt{3})/q_{100}$. Volume of the solvophobic chains $(v_{\rm L})$ has been calculated by the Tanford equation.³⁰

$$v_{\rm L} = 27.4 + 26.9N \tag{8}$$

where N is the number of carbon atoms in the hydrocarbon chain. The volume fraction (ϕ_L) has been deduced by the modifying equation mentioned by Yue et al. as water was used instead of ionic liquid.³¹

From the lattice parameter and volume fraction, $\phi_{\rm L}$, of the hydrophobic part of the surfactant in the system, some characteristic parameters are deduced.^{32,33} The radius, $d_{\rm H}$, of the hydrophobic part of the cylinders in the hexagonal structures was calculated using the following equation:

$$d_{\rm H} = \alpha' \sqrt{\frac{\sqrt{3}\,\phi_{\rm L}}{2\pi}} \tag{9}$$

The distance between the cylinders, d_{W} , is given by the relation

$$d_{\rm W} = \alpha' - 2d_{\rm H} \tag{10}$$

The effective cross-sectional area per surfactant at the interface, a_{S} , is calculated by the following equation

$$a_{\rm S} = \frac{2v_{\rm L}}{d_{\rm H}} \tag{11}$$

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where $v_{\rm L}$ is the volume of the apolar part of one surfactant molecule. The results of parameters α' , $d_{\rm H}$, $d_{\rm W}$, and $a_{\rm S}$ are summarized in Table 3.

Table 3. SAXS Da	ta for Hexa	gonal Liquid	Crystalline	Phases
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surfactant	surfactant (wt %)	water (wt %)	α' (Å)	d _w (Å)	d _H (Å)	a _s (Å ²)
12QuinucEsCl	50	50	54.3	16.1	19.1	36.7
	55	45	52.2	13.6	19.3	36.3
	60	40	49.4	11.4	19.0	36.9
	65	35	47.8	9.40	19.2	36.5
14QuinucEsCl	45	55	64.2	20.0	22.1	36.4
	50	50	61.5	16.7	22.4	36.1
	55	45	59.0	13.8	22.6	35.8

The ability of these surfactants to selectively form the hexagonal H_1 LC phase at high concentartion in water can be explained on the basis of interlocking of the quinuclidinolium headgroup. The molecular design of the quinuclidinolium headgroup enables them to self-aggregate in the aqueous system in such a manner in which the quinuclidinolium headgroups get interlocked among themselves.

The interlocking of the headgroups offers selectivity in only forming hexagonal H₁ LC phase in water since the flexibility to transit into different phases is inhibited. This is justified by the fact that the radius of the cylinder units $(d_{\rm H})$ and crosssectional area per surfactant at the interface $(a_{\rm S})$ do not significantly change with increase in percent of surfactant amount, and both the values have been found to be independent of the length of the hydrophobic alkyl chain. However, since the overall value of α' decreases, the water channel becomes more compact with increase in surfactant concentration. Since the rearrangement into different phases is restricted due to the headgroup interlocking of the surfactant molecules, with the increase in surfactant amount the system becomes unstable and often separates as solid surfactant above 66 wt % (in the case of 12QuinucEsCl) and 57 wt % (in the case of 14QuinucEsCl).

3.4. 1D and 2D NMR Studies of Quinuclidinolium Surfactants. The headgroup interlocking of the quinuclidinolium surfactants has been investigated in detail by 1D and 2D NMR spectroscopies. The ^IH NMR spectra of the quinuclidinolium surfactant (12QuinucEsCl) were recorded at different concentrations in D₂O (Figure 5). At 0.25 wt % (~6.43 mM) the majority of the surfactant molecules exist as monomers as the concentration is just above the cmc value and most of surfactant molecules are completely exposed to the solvent (D_2O) surface. The methylene protons (He and Hf) directly attached to the heterocyclic positively charged quinuclidinolium nitrogen which is present in-between quaternary nitrogen and ester bond undergo D₂O exchange (Figure 5a) at this concentration, and the proton signals are not observed. However, increasing the surfactant concentration causes gradual appearance of the He and Hf proton signals. At 0.40 and 0.50 wt % (~10.30 and ~12.88 mM, respectively) approximately half of the surfactant molecules exist as monomers whereas the rest exist in the form of micelles in D₂O. The interlocking of quinuclidinolium headgroup prevents the solvent D_2O from penetrating inside the micelle; consequently, the surfactant solution demonstrates partial D₂O exchange in NMR (Figure 5 b and c), and He and Hf proton signals are observed along with Hc and Hd proton signals as a multiplet. The merger of signal causes only a slight increase in the integration value accounting for the He and Hf protons which are part of the micelle. Further increase in the surfactant concentration results in the appearance of a new independent signal in ¹H NMR for He and Hf protons which merge with the signal of Hp proton above 2.5 wt %. At higher concentrations (above 2.5 wt %), most of the surfactants are present in the form of micelle and the interlocking of the quinuclidinolium headgroup does not allow the solvent to



Figure 5. ¹H NMR spectra of the quinuclidinolium surfactant (12QuinucEsCl) in D_2O at different concentrations at 25 °C: (a) 0.25, (b) 0.4, (c) 0.5, (d) 0.8, (e) 1.0, (f) 1.25, (g) 1.5, (h) 2.5, (i) 3.0, (j) 10.0, and (k) 30.0 wt %. Each individual proton is represented as colored balls as represented in the model in the right-hand side of the figure.



Figure 6. 2D NMR proton-proton correlation spectroscopy (COSY) of the quinuclidinolium surfactant (12QuinucEsCl) at (a) 1.5 wt % and (b) 30 wt % in D_2O at 25 °C. Each individual proton is represented as colored balls as represented in Figure 5



Figure 7. 2D nuclear Overhauser effect spectroscopy (NOESY) spectra of the quinuclidinolium surfactant (12QuinucEsCl) at (a) 1.5 wt % and (b) 30 wt % in D_2O at 25 °C. Each individual proton is represented as colored balls as represented in Figure 5

penetrate inside the micelle resulting in negligible D_2O exchange.

The increased concentration of the quinuclidinolium surfactants causes the chemical environment of the micellar surfactant solution to change which is evident from the downfield chemical shift of the observed protons. The protons directly attached to the quinuclidinolium headgroup experience more chemical shift compared to the protons which are part of the hydrophoblic alkyl chain. The results of the ¹H NMR spectroscopy strongly support the concept of quinuclidinolium headgroup interlocking; however, to understand the nature of such interlocking the quinuclidinolium surfactants were further investigated by 2D NMR (i.e., correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY)).

Homonuclear proton-proton correlation spectroscopy (COSY) experiments of the quinuclidinolium surfactant (12QuinucEsCl) were investigated at two different concentrations (i.e., 1.5 and 30 wt %, Figure 6a and b, respectively). The experiments gave direct information about the spin-spin coupling of each individual proton which is connected through chemical bonds. The assigned signals for the diastereotopic protons of each methylene group of quinuclidinolium headgroup (Figure 6a and b) are based on the analysis of the COSY cross-peaks. Additionally differentiation of each individual proton could be made from the heteronuclear ¹H-¹³C correlated spectra (HETCOR). At low concentration (Figure 6a), each of the diastereotopic protons of the quinuclidinolium headgroup directly attached to the positively charged quaternary nitrogen (i.e., HgHh, HkHl and HqHr) shows COSY cross-peaks demonstrating scalar couplings with the adjacent protons (i.e. HiHj, HmHn, and Hp) as well as among themselves. Such COSY cross-peaks are greatly affected with the increase in surfactant concentration in micellar region as HgHh, HkHl, and HgHr sets of protons demonstrate very weak (Figure 6b) or negligible spin-spin coupling at surfactant

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concentrations above 30 wt %. Since spin-spin coupling is a molecular internuclear interaction and depends on the molecular geometry of the molecule, the interlocking of the quinuclidinolium headgroup greatly influences the spin-spin coupling due to rigidness and change in chemical environment of the interlocked headgroup in the micellar system at high surfactant concentrations.

Nuclear overhauser effect spectroscopy (NOESY) provided further insight into the nature of interaction exhibited by the quinuclidinolium headgroups when they interlock among themselves in micellar solution (Figure 7a and b) as the associated cross-peaks in the spectra arise from the nuclei that are spatially or physically close and not connected to each other through chemical bond. At the low surfactant concentration (Figure 7a, the absence of cross-peaks in the spectra demonstrates that the nuclear Overhauser effect (NOE) is not prominent in dilute micellar solution; however, micellar solutions of higher concentrations above 30 wt % (Figure: 7b demonstrate significant NOE effect due to the quinuclidinolium headgroup interlocking.

The quinuclidine moiety can be considered having a twisted C_3 -symmetry³⁴ which has molecular cavities between the extended carbon arms. The similar carbon arm of adjacent quinuclidinolium moiety probably positions itself tightly in this cavity maintaining a distance due to electrostatic repulsion between similarly charged headgroups. Such arrangement in spherical system such as micelle results in interlocking of headgroups in a random manner where the protons of one quinuclidinolium moiety are spatially very close (less than 5 Å) to the other and may interact through dipole-dipole interaction.³⁵ However, the protons attached to carbon adjacent to the positively charged nitrogen of quinuclidinolium moiety (i.e., HgHh, HkHl, and HqHr) have been found to be spatially very close to similar protons of another quinuclidinolium moiety establishing highly ordered three-dimensional headgroup interlocking. Similarly, the protons attached to carbon at the β position from the quaternary nitrogen (i.e. HiHj, HmHn, and Hp) have been found to be close to similar protons of another quinuclidinolium moiety. Interestingly, the HOD proton has been found to be very close to Ho and Hp protons. It may be due to the formation of hydrogen bonding network possibly because quinuclidinolium moieties reorient anisotropically during headgroup interlocking which is supported by the fact that prominent downfield chemical shift has been observed for such micellar solutions (Figure 5). The free hydroxyl group of quinuclidinolium moiety may be responsible for the formation of intermolecular hydrogen bonding network between micellar systems with the help of water molecules in aqueous system, and such network further provides rigidity to the interlocked headgroups.

4. CONCLUSION

A new type of an ester-functionalized hydroxyl group containing quinuclidinolium surfactants has been synthesized starting from linear fatty alcohols and has been investigated by surface tension, conductivity, and SAXS experiments. The current research findings support the new concept of headgroup interlocking among quinuclidinolium headgroup which has been investigated in detail by 1D ¹H NMR, 2D proton–proton correlation spectroscopy (COSY), and nuclear Overhauser effect spectroscopy (NOESY). The dilute aqueous properties and liquid crystalline behavior of new quinuclidinolium surfactants are greatly influenced by the interlocking of headgroups. Such phenomena are able to primarily control the self-aggregation behavior of these surfactants in dilute aqueous solution since the entropic effect of transfer of the hydrocarbon chains from water into the interior of micelle is greatly affected. At the higher concentration the interlocked headgroup offers selectivity in forming a single type of liquid crystalline phase in water. The surface properties of these surfactants have been found to be better compared to commercially available conventional cationic surfactants. The ease of synthesis combined with biocompatible functional design and excellent surface properties makes them useful for several industrial and consumer applications.

ASSOCIATED CONTENT

Supporting Information

¹H, ¹³C NMR spectra, and HRMS data of the surfactants. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest

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