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ARTICLE

New Ester based Gemini Surfactants: Effect of Different Cationic Headgroups on Micellization Properties and Viscosity of Aqueous Micellar Solution

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A new series of ester functionalized cationic gemini surfactants having different cationic headgroups (i.e. piperidinium, pyrrolidinium, morpholinium and quaternary ammonium) have been synthesized and characterized using NMR and Mass spectroscopy. These new gemini surfactants were investigated for their micellization and viscosity properties using surface tension, conductivity, fluorescence and rheology thechniques. The physicochemical properties of the aqueous surfactant system were influenced by polarity, size and the the nature of cationic headgroups as the surface, thermodynamic and viscosity properties of these gemini surfactants were found to be dependent on the type of cationic headgroup. The current research finding establishes the structure-property relationship of the surfactant molecule specifically taking into account the dominant role displayed by the nature of cationic headgroup.

Introduction

Gemini surfactants are group of surfactant molecules consisting of two hydrophobic tail and two hydrophilic headgroups connected through a spacer unit (Figure 1a).[1,2] These surfactants are considered superior compared to their monomeric analogues (Figure 1b) due to their ability to aggregate as micelles in aqueous system at much lower concentration.[3] They are broadly classified into four categories depending on the types of headgroups (i. e. anionic, cationic, non-ionic and zwitterionic). Among them, cationic gemini surfactants consisting of two positively charged headgroups and two hydrophobic alkyl chains connected by a spacer are widely investigated category of gemini surfactants because of their unique ability to form complex with variety of negatively charged molecules/particles and surfaces available in nature.[4-6] The continued effort to improve the physicochemical properties of the gemini surfactant led to the development of many new gemini surfactants know as heterocyclic gemini surfactants (i.e. pyridinium,[7-11] pyrrolidinium,[12-14] imidazolium,[15-18] piperidinium,[19] and morpholinium[20]). These new gemini surfactants are currently being extensively investigated as they are considered as future surfactant molecule for many technical application areas.[21] In recent years, the field of surfactant science has witnessed robust transition and the use of surfactants for non-conventional application area has substantially increased. These application areas include use of surfactants as non-viral vectors for gene delivery,[22-24] drug delivery agent,[25] anti-microbial and anti-fungal agents,[26] soft template for the synthesis of mesoporous/microporous materials,[27] dispersants for carbon nanotubes, and capping agents for nanoparticles/nanomaterials.[28,29]

Gradually the biocompatibility and sustainability factor have also contributed to development and design of many new types of biocompatible surfactants containing biodegradable functional moieties such as ester[30,31] and amide groups,[32,33] which are often considered environmentally friendly because they can be easily degraded after their use.

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Figure 1: Basic molecular structure of (a) gemini surfactant and (b) monomeric surfactant.

Most of the studies concerning gemini surfactants are often conducted to investigate the role and/or effect of increase/decrease of either hydrophobic alkyl group or spacer length for a particular group of gemini surfactants, however the role of different cationic headgroups has seldom been investigated.[7-19] Furthermore, among the several categories of the cationic gemini surfactants the conventional gemini quaternary ammoniums,[34] gemini pyridinium,[7-11] gemini pyrrolidinium,[12-14] and gemini imidazolium[15-18] surfactants have been investigated in detail, however there are only few reports related to investigations concerning gemini piperidinium[19] and gemini morpholinium surfactant.[20] In this paper we have synthesized an entirely new series of ester functionalized cationic gemini surfactants containing different cationic headgroups (i. e. quaternary ammonium, piperidinium, pyrrolidinium and morpholinium) and investigated their role on self-aggregation properties. We noticed that the different cationic headgroups have appreciable impact on the solution properties of the surfactants, and physicochemical properties of surfactant solution can be tuned by varying the headgroups.

Experimental

Materials and Methods

Bromoacetic acid, dodecyl bromide, piperidine, pyrrolidine, morpholine and diethylamine were purchased from TCI, Tokyo, Japan. Detailed procedure for synthesis of gemini surfactants are described in supporting information. Millipore water was used in all experiments. Mass spectra of gemini surfactants were recorded on a JEOL JMS-T100CS (JEOL Japan) using ESI as ion source. ^{1}H-NMR and ^{13}C NMR spectra were recorded on JEOL-ECP500 (JEOL Japan) using CDCl$_3$ as solvent and tetramethylsilane (TMS) as an internal standard.

Surface Tension Measurements

The surface tension at water−air interface was investigated using the pendant drop technique (Kyowa Drop Master 700, Tokyo, Japan). An inverted 16-gauge needle is submerged in the aqueous phase such that the tip is visible in the frame of capture. Before the droplet is formed, the image capture software is triggered, collecting images at 90 frames for 30 min. Edge detection is used to identify the droplet shape, with the surface tension determined using the Young−Laplace equation. Experimental runs of 1800 s are chosen as surfactant solution attains equilibrium within the chosen time frame.[35,36]

Conductivity Measurements

Conductivity of the surfactant solution was measured using a 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 thermostated glass vessel controlled by a temperature controller. For the determination of the CMC value, 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.[37,38]

Fluorescence Measurements

The fluorescence intensities were measured using a Shimadzu RF-5300PC spectrofluorophotometer attached to a temperature controller water circulator. The individual surfactant solution of different concentrations was excited at 337 nm wavelength, and the emission spectra were recorded over the spectral range of 350-450 nm. The slit widths of excitation and emission were fixed at 1.5 and 1.5 nm, respectively. Initially pyrene solution was prepared by dissolving 20 mg of pyrene in 10 ml warm methanol. 40 µl of this solution was dissolved in 400 ml of Millipore water and stirred for 24 hours to prepare pyrene stock solution. The surfactant solutions of different concentrations were prepared using pyrene stock solution which were kept for 1 day at 25.0 °C to attain equilibration.[39]

Rheological Measurements

Viscosities of the aqueous surfactant solutions were measured using a stress-controlled rheometer, AR-G2 (TA Instruments) using cone-plate geometries (diameter 40 mm with cone angle of 2° 0′ 4″) attached to a temperature controller circulator. Samples were prepared in screw capped glass tubes by weighing appropriate surfactant and Millipore water. The tubes were sealed and kept at 80 ºC for 1 hour, then vortexed for 10 minutes and centrifuged at 3500rpm for 30 minutes. The procedure was repeated and the samples were kept for 24 hours to attain equilibrium. Steady-shear rheological measurements (viscosity vs shear-rate) were performed at 25℃. The zero-shear viscosity of the solutions was determined from steady shear rate measurements by extrapolating the viscosity in shear-rate curves to zero shear-rate.[40,41]
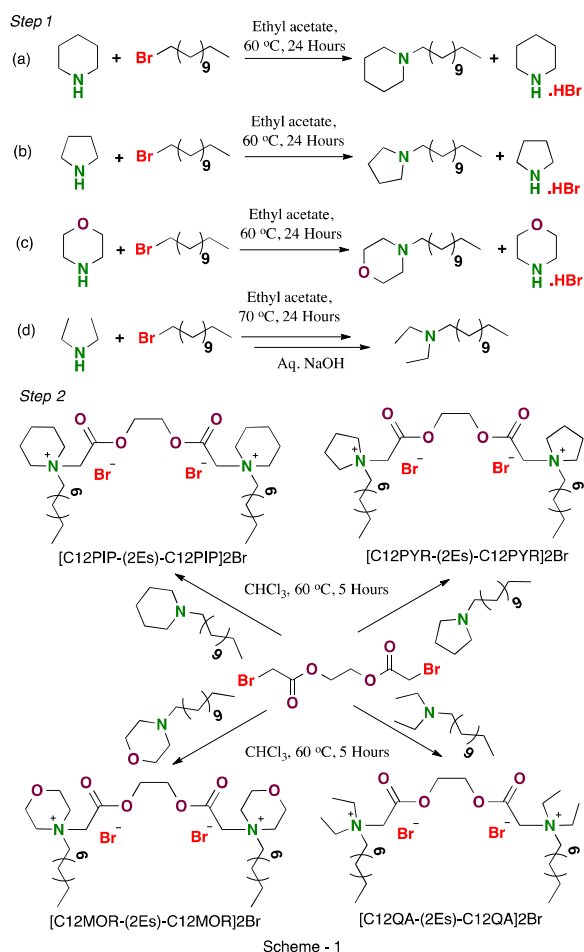
Results and discussion

Synthesis and Characterization

The new cationic gemini surfactants were synthesized in a two-step process (Scheme 1). Initially different heterocyclic and acyclic tertiary alkylamines ((i. e. 1-dodecylpiperidine, 1-dodecylpyrrolidine, 4-dodecylmorpholine and *N,N*-diethyldodecan-1-amine) were synthesized by reacting excess of individual amine (i. e. piperidine, pyrrolidine, morpholine and diethylamine) with dodecyl bromide.

Subsequent quaternization of respective heterocyclic and acyclic tertiary alkylamines with ethane-1,2-diyl bis(2-bromoacetate) gave corresponding gemini surfactants: 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpiperidin-1-ium) dibromide [C12PIP(2Es)C12PIP]2Br, 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpyrrolidin-1-ium) dibromide [C12PYR(2Es)C12PYR]2Br, 4,4'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(4-dodecylmorpholin-4-ium) dibromide [C12MOR(2Es)C12MOR]2Br and 2,2'-[ethane-1,2-diylbis(oxy)]bis(*N*-dodecyl-*N,N*-diethyl-2-oxoethanaminium) dibromide [C12QA(2Es)C12QA]2Br.

Scheme - 1

for the carbonyl carbon of ester group for these gemini surfactants were observed between δ 164.73 to 165.37 ppm for these gemini surfactant in ^{13}C NMR spectra.

The HRMS data obtained for these new gemini surfactants further helped to establish their chemical structure. The mass-to-charge ratio for these gemini surfactants [i.e. $(M^{2+}/2)+H$] were found to be 314.3063, 312.2874, 326.3079 and 328.2821 for [C12QA(2Es)C12QA]2Br, [C12PYR(2Es)C12PYR]2Br, [C12PIP(2Es)C12PIP]2Br and [C12MOR(2Es)C12MOR]2Br respectively, which were found to be very close to their calculated values. Apart from the distinguishing pattern observed for the mass-to-charge ratio for each individual surfactant, all these gemini surfactants demonstrated specific splitting pattern for breaking of ester bond in mass spectra.

Surface tension measurements

Surface properties of the new ester based cationic gemini surfactants were investigated by surface tension measurements. CMC corresponds to the point on the curve at which a sharp change of slope occurs. The fitting lines after the change in the slope and the fitting lines of the slope demonstrating decrease in surface tension intersect at certain point, which denotes CMC values of the surfactants (shown by arrows in Figure 2). The CMC values of these gemini surfactants were found to be dependent on the nature of the cationic headgroup and the polarity of headgroup significantly influences the CMC values of these gemini surfactants.
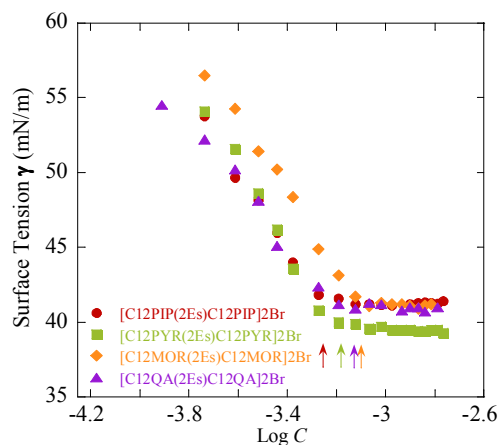
The chemical structures of the new cationic gemini surfactants were confirmed by NMR and high-resolution mass spectroscopy (HRMS). The resonance for the protons in between the positively charged quaternary nitrogen and ester functional group were observed as a singlet at δ 5.08, 5.17, 5.36 and 5.46 ppm for [C12QA(2Es)C12QA]2Br, [C12PIP(2Es)C12PIP]2Br, [C12PYR(2Es)C12PYR]2Br and [C12MOR(2Es)C12MOR]2Br respectively.

The chemical shifts for methylene protons of the spacer unit in-between two ester functionality are observed as singlet between δ 4.45-4.51 ppm for the gemini surfactants. Characteristic resonance signal for the protons directly attached to the quaternary nitrogen, which are part of hydrophobic alkyl chain length, were observed between δ 3.60-3.89 ppm for the gemini surfactants. The signals for the methylene protons adjacent to positively charged nitrogen, which are part of the heterocyclic ring were observed as two independent multiplets at δ 3.86 and 4.29 ppm for [C12PYR(2Es)C12PYR]2Br, but appeared as merged signal along with other protons between δ 3.72 and 4.47 ppm for [C12PIP(2Es)C12PIP]2Br and [C12MOR(2Es)C12MOR]2Br. However signal for the same set of protons for acyclic quaternary ammonium surfactant: [C12QA(2Es)C12QA]2Br appeared as characteristic quartet at δ 3.85 ppm integrating for eight protons. The characteristic signals

Figure 2: Surface tension vs log C plot for the cationic gemini surfactants.

Piperidinium headgroup consisting of six membered heterocyclic ring containing five methylene bridges attached to one positively charged nitrogen can be considered as the least polar headgroup among the series of gemini surfactants investigated followed by the pyrrolidinium headgroup (five membered heterocyclic) containing four methylene bridges attached to one positively charged nitrogen and quaternary ammonium gemini surfactant. In contrast, the morpholinium headgroup consisting of six membered heterocyclic ring containing two heteroatoms i.e. one oxygen (as ether functionality) and one positively charged nitrogen is the most polar and least hydrophobic headgroup

investigated in the current studies. Heterocyclic cationic gemini surfactant having piperidinium headgroup: [C12PIP(2Es)C12PIP]2Br has the lowest CMC value while the gemini surfactant having morpholinium headgroup: [C12MOR(2Es)C12MOR]2Br has highest CMC value among the series of gemini surfactants although both surfactants have six membered heterocyclic ring as headgroup. The CMC values of these gemini surfactants decreases as [C12PIP(2Es)C12PIP]2Br > [C12PYR(2Es)C12PYR]2Br > [C12QA(2Es)C12QA]2Br > [C12MOR(2Es)C12MOR]2Br. It is interesting to note that the heterocyclic pyrrolidinium gemini surfactant: [C12PYR(2Es)C12PYR]2Br closely resembles its structural analogue [C12QA(2Es)C12QA]2Br: a quaternary ammonium gemini surfactant having two ethyl groups attached to the positivity charged nitrogen with a difference, as the former is a closed cyclic system and the later a noncyclic gemini surfactant. However the CMC values of these surfactants significantly differ from one another as the CMC value of [C12PYR(2Es)C12PYR]2Br is lower compared to [C12QA(2Es)C12QA]2Br. The other surface properties i.e. effectiveness of surface tension reduction (γ_{min}) at the CMC, surface excess concentration (Γ_{CMC}), surface area occupied by molecule at air/water interface (A_{min}), efficiency in surface tension reduction by 20 mN.m^{-1} (C_{20}) were deduced from the surface tension plot of the gemini surfactants (Table 1).

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

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

Here, γ denotes the surface tension, R is the gas constant, T is the absolute temperature, and C is the surfactant concentration. The n is a constant, which depends on the number of individual ions comprising the surfactant that are adsorbed at the interface. For gemini surfactants the value of n is 3, therefore the value of n is taken as 3.[41] The continual adsorption of the surfactant monomers at the air-water interface with increasing surfactant concentration causes the surface tension of the aqueous system to gradually decrease. The constant adsorption of the surfactants results in active accumulation at the interface and the concentration of the surfactant monomers becomes more

concentrated at the interface compared to bulk solution. Γ_{max} signifies the area associated with the concentration of the gemini surfactant at the air-water interface and its value depends on the nature and size of the cationic headgroups. Six membered heterocyclic headgroups (piperidinium amd morpholinium) have higher Γ_{max} compared to five membered heterocyclic headgroup (pyrrolidinium) and the acyclic quaternary ammonium headgroup has the lowest Γ_{max} value. The area occupied per surfactant molecule (A_{min}) at the air-water interface[41] is obtained by using the following equation:

$$A_{min} = 1/N\Gamma_{max} \qquad (2)$$

where N is Avogadro's number and A_{min} is in nm^2. The values of Γ_{max} and A_{min} are shown in Table 1. The A_{min} values of all the heterocyclic gemini surfactants ([C12PIP(2Es)C12PIP]2Br, [C12PYR(2Es)C12PYR]2Br and [C12MOR(2Es)C12MOR]2Br) have been found to be lower compared to the quaternary ammonium gemini surfactant: [C12QA(2Es)C12QA]2Br, however we have found that the different types of heterocyclic headgroup have very little impact on the calculated A_{min} values. Significant difference in calculated A_{min} values can be observed for [C12QA(2Es)C12QA]2Br compared to its structural analogue having methyl group attached to quaternary nitrogen. [C12QA(2Es)C12QA]2Br having ethyl groups attached to the quaternary ammonium group has higher A_{min} value than the similar ester functionalized gemini surfactants having methyl group attached to quaternary ammonium group as well as conventional quaternary ammonium gemini surfactants.[35] The calculated A_{min} values of the ester based pyrrolidinium gemini surfactant: [C12PYR(2Es)C12PYR]2Br were less compared to its structural analogues.[9-11] Interestingly both the six membered heterocyclic surfactants having piperidinium and morpholinium cationic headgroups (i. e. [C12PIP(2Es)C12PIP]2Br and [C12MOR(2Es)C12MOR]2Br) have the lowest A_{min} values, signifying the impact of size of cationic headgroup on the calculated parameter.

γ_{min} is the maximum ability of the surfactant to reduce surface tension of the water close to CMC value. The surfactant monomers adsorb at the air-water interface and reduce the surface tension of the water. At certain point the entire interface is completely occupied by the surfactant monomers and further increasing the surfactant concentration does not bring further decrease in the surface tension of the aqueous system. At this

Table 1. Surface properties of gemini surfactants as determined by Surface Tension Measurements.

Surfactant	cmc^a (mM)	cmc^b (mM)	cmc^c (mM)	γ_{cmc} (mN.m^{-1})	$10^6\Gamma_{max}$ (mol.m^{-2})	A_{min} (nm^2)	C_{20} (M)
[C12PIP(2Es)-C12PIP]2Br	0.56 (±0.02)	0.60 (±0.01)	0.58 (±0.01)	41.6 (±0.2)	1.48 (±0.02)	1.12 (±0.02)	2.09×10^{-4}
[C12PYR(2Es)-C12PYR]2Br	0.67 (±0.02)	0.73 (±0.01)	0.69 (±0.01)	40.0 (±0.2)	1.39 (±0.02)	1.19 (±0.02)	2.24×10^{-4}
[C12MOR(2Es)-C12MOR]2Br	0.79 (±0.02)	0.96 (±0.01)	0.93 (±0.01)	41.1 (±0.2)	1.46 (±0.02)	1.14 (±0.02)	3.02×10^{-4}
[C12QA(2Es)-C12QA]2Br	0.75 (±0.02)	0.92 (±0.01)	0.79 (±0.01)	40.9 (±0.2)	1.02 (±0.02)	1.63 (±0.02)	1.78×10^{-4}

cmc^a determined by surface tension method, cmc^b determined by conductivity method and cmc^c determined by fluorescence method.

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particular point the slope of the surface tension curve suddenly changes and becomes constant and the corresponding point is referred as γ_{min}. The γ_{min} values of the new gemini surfactants depends on the nature of the cationic headgroup. Gemini pyrrolidinium surfactant: [C12PYR(2Es)C12PYR]2Br is able to decrease the surface tension of water to greater extent compared to other members of the series.

C_{20} is the concentration of the surfactant required to decrease the surface tension of the aqueous system by 20 mN.m^{-1} and gives information about the effectiveness of individual surfactant to lower surface tension when present at very low concentration. We have noticed that the quaternary ammonium gemini surfactant: [C12QA(2Es)C12QA]2Br have lower C_{20} value compared to heterocyclic gemini surfactants: [C12PIP(2Es)C12PIP]2Br, [C12PYR(2Es)C12PYR]2Br and [C12MOR(2Es)C12MOR]2Br.

Conductivity Measurements

The surface and thermodynamic properties of the gemini surfactants have been investigated by conductivity method. The determined CMC values were in close agreement with those determined by surface tension measurements and similar trend has been observed. The CMC values of these new ester based

gemini surfactants are comparable to other heterocyclic cationic gemini surfactants i. e. pyridinium, imidazolium, pyrrolidinium surfactants as well as conventional quaternary ammonium gemini surfactants and these gemini surfactants are equivalently good as other recently developed gemini surfactants.[7-18] However the main focus of our current study is to investigate the effect of different cationic headgroups on self-aggregation and thermodynamic properties, which has seldom been investigated.

The specific conductivity data of these new gemini surfactants in aqueous solutions investigated at different temperatures (Figure 3) were helpful in deducing the self-aggregation and thermodynamic data for these new surfactants with different headgroups (Table 2). We have noticed that the nature of headgroup influences the aggregation behavior of the surfactants in aqueous solution.

The degree of counterion binding (β) which represents the negatively charged counterions associated with the micelles in aqueous solution can be calculated from the following equation:

$$\beta = 1 - (S_{micellar}/S_{premicellar}) \qquad (3)$$

Where $S_{micellar}$ is the slope after the CMC value and $S_{premicellar}$ is the slope before the CMC value. The calculated β values for the gemini surfactants represents the bromide counter ions that are
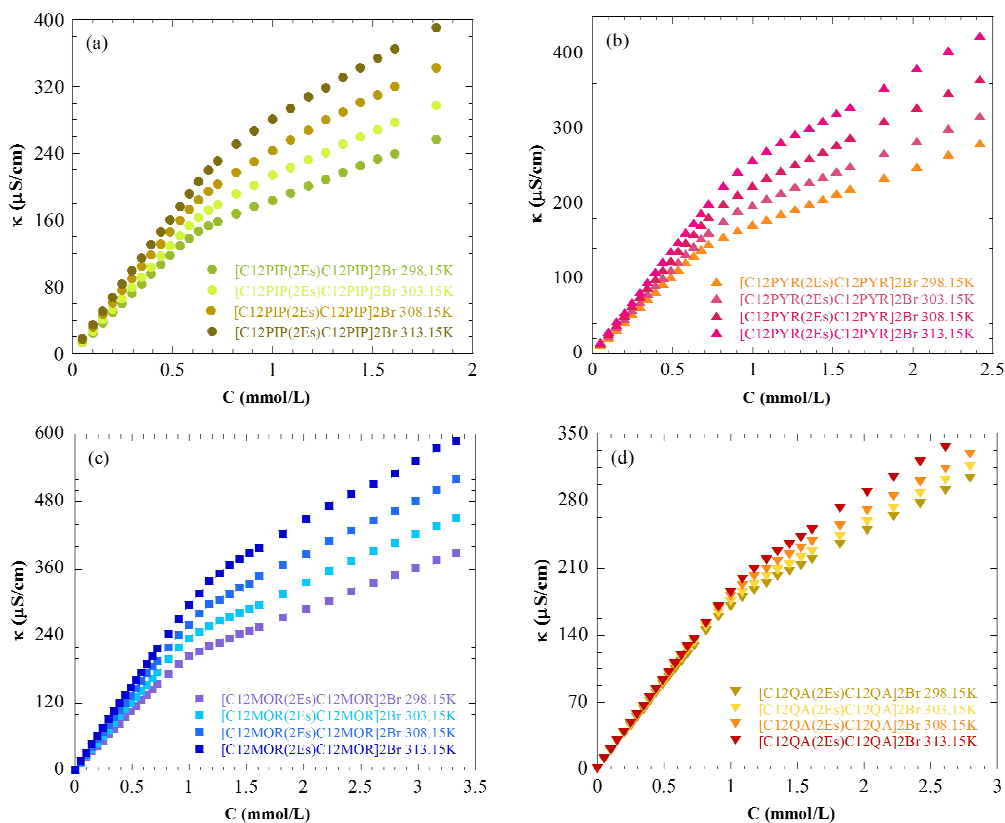

Figure 3: Specific conductivity versus concentration plot of gemini surfactants (a) [C12PIP(2Es)C12PIP]2Br (b) [C12PYR(2Es)C12PYR]2Br (c) [C12MOR(2Es)C12MOR]2Br and (d) [C12QA(2Es)C12QA]2Br at different temperatures.

present in the Stern layer of the micelles to counterbalance the electrostatic force that opposes micelle formation. Recent studies show that β values of gemini surfactants are typically independent and does not follow any particular trend and are often independent of change in length of spacer units, hydrophobic alkyl chain length and nature of counterions.[7-18] Since aggregation of monomers into micelles is not solely dependent on electrostatic force but on the combination of other forces i.e. the van der Waals interaction or hydrophobic interactions, the repulsion between similarly charged headgroups, the hydrophobic hydration, and the energetics associated with the configuration of the spacer chain. Therefore, β values deduced from the slopes of conductivity data are helpful in calculating the overall thermodynamic properties of the surfactants. We have noticed that the β values of the heterocyclic gemini surfactants do not vary much with change in the type of heterocyclic headgroups. This may be attributed to the fact that the molecular design of the gemini surfactants is almost similar i.e. hydrophobic chain length, spacer length and counterions, therefore the contributions arising from the change in headgroup
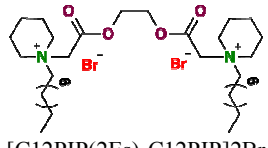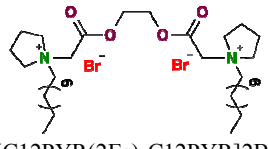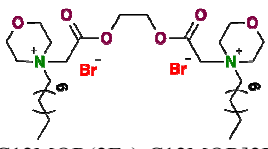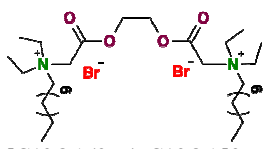
have very little impact on the calculated parameter. However when compared to non-heterocyclic structural analogue of these new surfactants i.e. [C12QA(2Es)C12QA]2Br, the β shows change which may be due to contributions arising from the acyclic headgroup which is typically different to heterocyclic analogues. The β values of these new ester based gemini surfactants decrease with increase in temperature.

The Gibbs free energy for micellization (ΔG^0_{mic}) denoting the work done to transfer the monomeric form of surfactants from the air-water interface to the micellar phase in the bulk solution is calculated from the following equation:

$$\Delta G^0_{mic} = RT(0.5 + \beta) \ln X_{CMC} \qquad (4)$$

Where R is the gas constant (8.314 J mol^{-1} K^{-1}); T is absolute temperature; X_{CMC} is the CMC in molar fraction, X_{CMC} = CMC/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 ºC. β is the degree of counterion binding to micelles. Micellization of new gemini surfactants is a spontaneous process as the calculated values for ΔG^0_{mic} are negative. The free energy for micellization

Table 2: The cmc values and thermodynamic parameters of gemini surfactants determined by the electrical conductivity method at different temperatures.

Surfactant	T (ºC)	cmc (mM)	β	ΔG^0_{mic} kJ.mol^{-1}	ΔG^0_{ads} kJ.mol^{-1}	ΔH^0_{mic} kJ.mol^{-1}	$T\Delta S^0_{mic}$ kJ.mol^{-1}
[C12PIP(2Es)-C12PIP]2Br	25±0.1	0.60 (±0.01)	0.61	-31.5 (±0.2)	-52.0 (±0.2)	-14.3 (±0.2)	17.2 (±0.2)
	30±0.1	0.66 (±0.01)	0.59	-31.2 (±0.2)		-14.6 (±0.2)	16.6 (±0.2)
	35±0.1	0.72 (±0.01)	0.58	-31.1 (±0.2)		-14.9 (±0.2)	16.2 (±0.2)
	40±0.1	0.78 (±0.01)	0.58	-31.4 (±0.2)		-15.4 (±0.2)	16.0 (±0.2)
[C12PYR(2Es)-C12PYR]2Br	25±0.1	0.73 (±0.01)	0.63	-31.5 (±0.2)	-54.5 (±0.2)	-10.6 (±0.2)	20.9 (±0.2)
	30±0.1	0.78 (±0.01)	0.62	-31.5 (±0.2)		-10.9 (±0.2)	20.6 (±0.2)
	35±0.1	0.84 (±0.01)	0.60	-31.3 (±0.2)		-11.0 (±0.2)	20.3 (±0.2)
	40±0.1	0.88 (±0.01)	0.58	-31.1 (±0.2)		-11.2 (±0.2)	19.9 (±0.2)
[C12MOR(2Es)-C12MOR]2Br	25±0.1	0.97 (±0.01)	0.63	-30.7 (±0.2)	-51.9 (±0.2)	-11.6 (±0.2)	19.1 (±0.2)
	30±0.1	1.07 (±0.01)	0.62	-30.6 (±0.2)		-11.9 (±0.2)	18.7 (±0.2)
	35±0.1	1.13 (±0.01)	0.61	-31.7 (±0.2)		-12.1 (±0.2)	19.6 (±0.2)
	40±0.1	1.20 (±0.01)	0.61	-31.0 (±0.2)		-12.5 (±0.2)	18.5 (±0.2)
[C12QA(2Es)-C12QA]2Br	25±0.1	0.92 (±0.01)	0.58	-29.5 (±0.2)	-61.7 (±0.2)	-9.5 (±0.2)	20.0 (±0.2)
	30±0.1	0.97 (±0.01)	0.57	-29.5 (±0.2)		-9.7 (±0.2)	19.8 (±0.2)
	35±0.1	1.03 (±0.01)	0.56	-29.6 (±0.2)		-10.0 (±0.2)	19.6 (±0.2)
	40±0.1	1.10 (±0.01)	0.52	-28.8 (±0.2)		-9.9 (±0.2)	18.9 (±0.2)

for the heterocyclic gemini surfactants does not significantly change with the change in the cationic headgroups and the parameter has little dependence on the nature of heterocyclic headgroups. However, the quaternary ammonium analogue [C12QA(2Es)C12QA]2Br has absolutely lower ΔG^0_{mic} value compared to its heterocyclic derivatives.

The Gibbs free energy of adsorption (ΔG^0_{ads}) symbolizes the free energy to transfer surfactant in solution to the air-water interface and is calculated by the following equation:

$$\Delta G^0_{ads} = \Delta G^0_{mic} - \frac{\pi_{cmc}}{\Gamma} \qquad (5)$$

Here, π_{CMC} denotes the surface pressure at the CMC ($\pi_{CMC} = \gamma_o - \gamma_{CMC}$, where γ_o and γ_{CMC} are the surface tensions of water and the surfactant solution at CMC, respectively).

ΔG^0_{ads} of these gemini surfactants depends upon the nature of cationic headgroup and its absolute value generally decreases as [C12QA(2Es)C12QA]2Br > [C12PYR(2Es)C12PYR]2Br > [C12PIP(2Es)C12PIP]2Br > [C12MOR(2Es)C12MOR]2Br. The quaternary ammonium gemini surfactant: [C12QA(2Es)C12QA]2Br has the lowest negative value of ΔG^0_{ads} suggesting that this surfactant has the highest ability to adsorb at the air-water interface followed by gemini pyrrolidinium surfactant: [C12PYR(2Es)C12PYR]2Br. It has been observed that the heterocyclic gemini surfactants have lower absolute value of ΔG^0_{ads} compared to the acyclic quaternary ammonium derivative and the values also depend on the size of heterocyclic ring. Both the six membered piperidinium and morpholinium headgroup have almost similar and lowest absolute values of ΔG^0_{ads}, which increases for pyrrolidinium derivative, a five membered heterocyclic moiety.

The standard enthalpy change for micellization process (ΔH^0_{mic}) can be determined using the Gibbs-Helmholtz equation:

$$\Delta H^0_{mic} = \left(\frac{\partial (\Delta G^0_{mic} / T)}{\partial (1/T)} \right) \qquad (6)$$

The standard entropy of micelle formation (ΔS^0_{mic}) can be calculated according to the following equation:

$$T\Delta S^0_{mic} = \Delta H^0_{mic} - \Delta G^0_{mic} \qquad (7)$$

Negative value of ΔH^0_{mic} signifies that the micellization is an exothermic process. The calculated ΔH^0_{mic} value significantly depends on the nature of the cationic headgroups. Both the size and the polarity of the cationic headgroups significantly influence the ΔH^0_{mic} values of these new gemini surfactants. The absolute value of ΔH^0_{mic} decreases as shown: [C12PIP(2Es)C12PIP]2Br > [C12MOR(2Es)C12MOR]2Br > [C12PYR(2Es)C12PYR]2Br > [C12QA(2Es)C12QA]2Br. Both the gemini surfactants containing six membered heterocyclic ring have larger absolute ΔH^0_{mic} value compared to other gemini surfactants, however it is interesting to note that there is a sharp decrease in the calculated ΔH^0_{mic} value from the piperidinium gemini surfactant to the morpholinium gemini surfactant. This can be explained on the basis of nature of the cationic

headgroups. The contributions arising because of van der Waals interactions between the hydrophobic alkyl chains; repulsions between similar charged headgroup; and rearrangements due to spacer units are theoretically same for both the gemini surfactants, however the morpholinium headgroup is relatively more polar compared to the piperidinium headgroup because of the presence of oxygen in the form of cyclic ether linkage. Therefore the observed difference in the calculated ΔH^0_{mic} values may be associated with the difference in hydration of the cationic headgroups.[30] Recent reports suggest that the formation of hydrogen bonds between the polar functional groups has marked effect on the process of micelle formation since the nature of force in display is much stronger than the van der Waals interactions. It is quite possible that the nonbonding electrons on the oxygen atom of morpholinium ring are able to form hydrogen bonding with water molecules and is able to influence the thermodynamic parameters of the surfactant system. The lower absolute ΔH^0_{mic} value for [C12QA(2Es)C12QA]2Br can be attributed to the greater flexibility of the quaternary ammonium headgroup compared to other heterocyclic headgroups. The steric hindrance in micelle formation originating from the nature of headgroup is minimum for the quaternary ammonium headgroup in which the ethyl groups are attached to the positively charged nitrogen (because of their greater flexibility), however steric factors are more pronounced in case of the other heterocyclic moieties. The micellization process for the gemini surfactants under investigation has been found to be entropy driven for all these gemini surfactants since the value for standard entropy of micelle formation ($T\Delta S^0_{mic}$) is larger than the enthalpy changes for all the gemini surfactants.

CMC by Fluorescence Method

The CMC value of the gemini surfactants is further investigated by the fluorescence method using pyrene as probe. The fluorescence spectrum of pyrene in water exhibits five predominant peaks and the ratio of intensity of the first (I_1 at 373nm) and third peaks (I_3 at 384nm) is a sensitive to the probe's
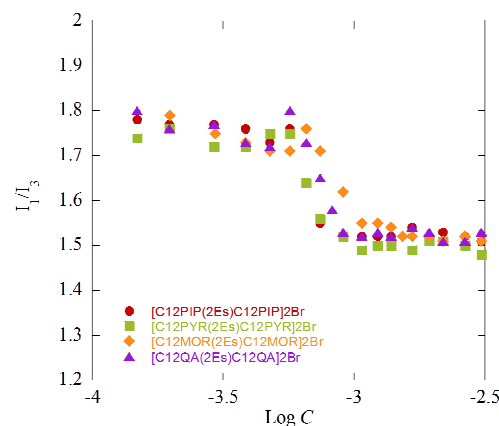

Figure 4: Plot of the I_1/I_3 ratio of the pyrene versus log of concentration of the aqueous solution of the gemini cationic surfactants at 25 ºC.

environment.[42] The solubilization of the pyrene in the micelles causes the microenvironment of the system to change and fluorescence emission spectra give useful information about the aggregation occurring in the aqueous solutions. I_1/I_3 is almost constant if no micellar aggregate is present in the solution since the fluorescence probe is completely exposed in the solution, however as the interface becomes completely occupied by the surfactant monomers the surfactant molecules start aggregating as micelles and this causes sigmoidal drop in the I_1/I_3 intensity. The change in the microenvironment of the surfactant-pyrene solution can be observed in the form of changes occurring in the fluorescence spectra and the intensity ratio of the first and third peak i.e. I_1/I_3 ratio is taken as a measure for determining the CMC values of the surfactants. This phenomenon is caused by the change in the microenvironment of the system as some of the probe molecules are trapped inside the surfactant micelle. The plot of I_1/I_3 versus concentration (Figure 4) forms a reverse sigmoid curve and the center point in the sigmoid decrease is often considered as critical micelle concentration.[43] The CMC values of [C12PIP(2Es)C12PIP]2Br, [C12PYR(2Es)C12PYR]2Br, [C12MOR(2Es)C12MOR]2Br and [C12QA(2Es)C12QA]2Br have found to be 0.58, 0.69, 0.93 and 0.79 respectively (Table 1). The observed I_1/I_3 values of these ester functionalized gemini surfactants above their CMC values have been found to be relatively higher compared for other

gemini surfactants.[44-47] This may be attributed to the presence of the polar ester functionality as spacers since similar behavior has been observed for other ester functionalized gemini surfactants.[31]

Viscosity of Aqueous Surfactant Solutions

Rheological measurement (viscosity (η) vs. shear-rate (γ)) was performed for the aqueous surfactant solutions of the gemini surfactants at different concentrations (i.e. 10wt%, 20wt%, 30wt% and 40wt%) at 25 °C and the results of the experiments are shown in Figure 5(a-d). The viscosity of the aqueous surfactant solution increased with the increase in the concentration of the gemini surfactants and the viscosity of each individual surfactant solution significantly depends on the nature of the cationic headgroups. The aqueous surfactant solutions of [C12PYR(2Es)C12PYR]2Br with pyrrolidinium headgroup demonstrate higher viscosity from 10wt% to 40wt% compared to other category of the gemini surfactants while the gemini morpholinium surfactants has the lowest observed viscosity at the same concentration. At 10wt% the aqueous surfactant solutions of the all the gemini surfactants demonstrated very little difference in the observed rheological behavior except the aqueous solution of the gemini morpholinium surfactant, which showed lower viscosity at the same concentration. The aqueous solution of the gemini surfactants demonstrated cationic headgroup dependent viscosity behavior which decreases as
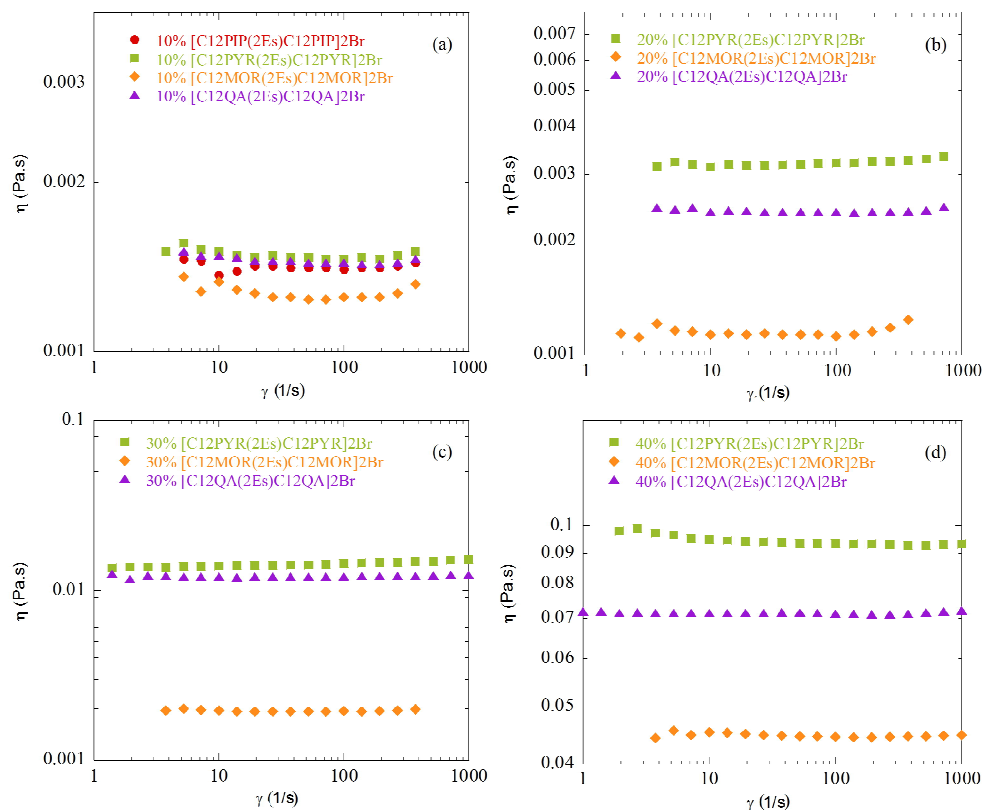

Figure 5: Viscosity vs. steady shear rate curves for (a) 10 wt% (b) 20wt% (c) 30wt% and (d) 40wt% aqueous solution of the gemini surfactants with different cationic headgroup.

[C12PYR(2Es)C12PYR]2Br >[C12QA(2Es)C12QA]2Br> [C12PIP(2Es)C12PIP]2Br > [C12MOR(2Es)C12MOR]2Br, however the first three members shown in the trend does not significantly differ from one another.

Piperidinium gemini surfactant: [C12PIP(2Es)C12PIP]2Br cannot be investigated above 20wt% because of its limited solubility at higher surfactant concentrations. Above 20wt% the observed rheological properties significantly differ from one another and the viscosity of the aqueous surfactant solutions of the gemini surfactants decreases as [C12PYR(2Es)C12PYR]2Br > [C12QA(2Es)C12QA]2Br> > [C12MOR(2Es)C12MOR]2Br. It can be observed that for all these gemini surfactants the viscosities remain almost constant with the increase in the shear rate, thus the aqueous solutions of all these ester functionalized gemini surfactants show Newtonian fluid behavior. The rheological properties of these new gemini surfactants with the ester functional group significantly differ from the conventional quaternary ammonium gemini surfactants although the complete comparison is not possible as the later group of surfactants demonstrate both Newtonian and non-Newtonian fluid behavior depending on the length of the hydrophobic alkyl chain and spacer.[48] The morpholinium gemini surfactant: [C12MOR(2Es)C12MOR]2Br demonstrated lower viscosity compared to the other gemini surfactant solutions. This property may be attributed to the presence of additional heteroatom oxygen in heterocyclic group in addition to the two-ester functionality that is present in all the surfactants. Earlier the micellization in aqueous solution was thought to be principally dependent on the hydrophobic effect. However, most recent reports suggest the importance of the polar functional groups in the self-aggregation of amphiphilic molecules in water via formation of hydrogen bonding.[49-52] The presence of this polar ether linkage in the morpholinium headgroup in addition to ester group may result in formation of hydrogen bonding between the nonbonding electrons on oxygen atom and water molecules, which ultimately influence not only the thermodynamic behavior but also the rheological behavior of the surfactants. Furthermore, the gemini morpholinium surfactant demonstrated unique ability to exist as micellar solution up to 50 wt% in water at low temperature (15ºC) which makes it ideal for several low temperature applications.

Conclusions

An entirely new series of cationic gemini surfactants with different cationic headgroups have been synthesized and characterized using spectroscopic techniques. We have found that both the self-aggregation and the viscosity properties of these gemini surfactants are influenced by the nature of cationic headgroups. The CMC values along with the other surface parameters (i.e. γ_{min}, Γ_{CMC}, A_{min}, C_{20} values) of these gemini surfactants significantly differ from one another depending upon the type of headgroup. Further, the thermodynamic parameters (ΔG^{o}_{mic}, ΔG^{o}_{ads}, ΔH^{o}_{mic} and $T\Delta S^{o}_{mic}$) were also significantly influenced depending on the nature of the cationic headgroups.

The aqueous solutions of gemini surfactants were further investigated for their viscosity properties at various concentrations and the results demonstrated that the observed viscosity considerably depend on the concentration as well as the nature of the cationic headgroups. The gemini morpholinium surfactant having an additional oxygen heteroatom besides the positively charged nitrogen atom demonstrated a higher CMC value and lower viscosity compared to the other category of the gemini surfactants. Our results show that the physicochemical properties of the gemini surfactants can be varied by not only the change in the hydrophobic alkyl length or spacer length but also by varying the type of cationic headgroup. The surface properties and the viscosity of the aqueous solutions of the gemini surfactants can be tuned to desired values by just varying their headgroup and keeping the length of spacer and hydrophobic tail constant.

Acknowledgements

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