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Studies on Synthesis, Characterization, Micellar Features, and Solubilization of Four Novel Cationic Gemini Surfactants

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molar solubilization ratio (MSR). Additionally, the emulsification powers have been measured.

1. INTRODUCTION

Micellization and self-assembly, which are natural and spontaneous processes, occur primarily owing to noncovalent interactions.¹ Surfactants are an amphiphilic molecule containing a hydrophobic tail and a hydrophilic head group.² Surfactants have attracted great interest because of their properties associated with suspension, efficient solubilization, transport, and dispersion.³ In an aqueous solution, above their critical micelle concentration (cmc), some kind of selforganizing molecular assembly can be formed from surfactants. Surfactants are significant for the scientific world and have many application areas in industry and laboratories. Agrochemical, pesticides, textile, cosmetics, herbicides, biotechnology, detergents, pharmaceuticals, medicals, mineral flotation, food processing, nanotechnology, paint, petroleum, drug delivery, improved oil recovery, and agriculture are some surfactant applications commonly used in industry.⁴⁻¹⁰

Gemini surfactants (GSs) have attracted great attention after the 2000s, especially due to their aggregation properties.¹¹ They are a category of amphiphilic compounds that are a novel and important topic for colloids and surface sciences. GSs have practices that are more functional in preparation of mesoporous materials, corrosion inhibitors, oil recovery, phase transfer catalysts, polymerization, biomedical applications, DNA extraction, drug delivery, gene delivery, and as germicides.^{12–20} They occur from two amphiphilic parts. A small, long, rigid, or stretchy spacer attaches these two amphiphilic parts at the level or very close to the head groups.²¹ The tail length of surfactants and the breadth between two heads are the two main factors affecting micellization and micellar characters in conventional surfactant micelles. Additionally, the spacer length and type are also substantial factors in gemini micelles.²² Consequently, the aggregation behavior of GS can be efficiently adjusted by arranging the spacer groups. Detailed research studies have indicated that the nature of spacer severely influences the surface activity and aggregation behavior in GSs.²³ GSs present interesting physical-chemical characteristics. Compared with the conventional surfactants, GSs have a much lower cmc.²⁴ GSs are more surface-active compared to their parent monomeric counterparts.²⁵ These features further have increased the attention in GSs.²⁶

With the advancement in industrial technology, higher performance surface-active compounds are required.²⁷ For this reason, it is very important to conduct studies on the determination of physicochemical properties of novel gemini species with high surface activity. Bis-quaternary ammonium compounds have an important place among gemini surfactants

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Table 1. Properties of the Chemicals Used in This Stud	ly
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chemical name	mass fraction c	hemical formula	CAS Reg. No.	suppliers
dodecanoyl chloride	99%	C ₁₂ H ₂₃ ClO	112-16-3	Sigma-Aldrich
3-(1H-imidazol-1-yl)propan-1-amine	97%	$C_6H_{11}N_3$	5036-48-6	Sigma-Aldrich
1,4-dibromobutane	99%	$C_4H_8Br_2$	110-52-1	Sigma-Aldrich
1,6-dibromohexane	96%	$C_6H_{12}Br_2$	629-03-8	Sigma-Aldrich
ethylene glycol	99.5%	$C_2H_6O_2$	107-21-1	Merck Millipore
1,4-butanediol	99%	$C_4H_{10}O_2$	110-63-4	Sigma-Aldrich
bromoacetyl bromide	98%	C_2H_3BrO	598-21-0	Sigma-Aldrich
ethanol (absolute)	99.9%	C ₂ H ₅ OH	64-17-5	Merck Millipore
paraffin oil			8012-95-1	Sigma-Aldrich
chloroform	for analysis	CHCl ₃	67-66-3	Sigma-Aldrich
dichloromethane	99.8%	CH_2Cl_2	75-09-2	Sigma-Aldrich
potassium carbonate	≥99.0%	K ₂ CO ₃	584-08-7	Merck Millipore
calcium chloride (anhydrous)	≥93.0%	CaCl ₂	10043-52-4	Sigma-Aldrich
pyridine	≥99.0%	C ₅ H ₅ N	110-86-1	Sigma-Aldrich
sodium bicarbonate	≥99.7%	NaHCO ₃	144-55-8	Merck Millipore

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that have been studied extensively by researchers. The reason why such compounds are so important may be that cationic gemini surfactants (CGSs) with unique surface-active features can be prepared by relatively easy synthetic methods and with high chemical yields.²⁸ In recent years, a few new CGS groups based on pyridinium, imidazolium, pyrrolidinium, piperidi-nium, and amino acid²⁹⁻³³ have been developed and studied. Compared to conventional surfactants, imidazolium-based GSs present additional contributions as they contain imidazolium head groups. These types of gemini surfactants have potential applications in biology because there is a strong attraction among aromatic rings of imidazolium head groups owing to the $\pi-\pi$ interaction.³⁴ In addition, the group of gemini surfactants containing degradable amide bonds in various parts of their structure has also received exclusive interest. Amide bonding affects both the biodegradability of surfactants and their aggregation in aqueous solution.¹¹ The geminis are made more cleavable/biodegradable with lower aquatic toxicity than other cationic surfactants by ester bonding in the spacer. Geminis become degradable owing to the polar bond that increases water solubility.33

In this article, four novel imidazolium-based CGSs have been synthesized, purified, and characterized. Research studies on micellar and solubilization features of CGSs have been conducted. The parameters, namely, cmc, α (counterion dissociation degree), β (counterion binding degree), $\Delta G_{\rm mic}^{\circ}$ (standard Gibbs free energy change), $\Delta H_{\rm mic}^{\circ}$ (enthalpy change), $\Delta S_{\rm mic}^{\circ}$ (standard entropy change), and MSR (molar solubilization ratio), for CGSs have been calculated. The emulsification efficiencies of CGSs have been measured. By comparing the data for these CGSs, the effects of changing the number of carbon or oxygen atoms in the spacer on solution features in micelle formation have been identified. It has been also investigated how the spacer nature affects the Krafft temperature ($T_{\rm K}$).

2. EXPERIMENTAL PROCEDURES

2.1. Materials. Dodecanoyl chloride (99%), 3-(1*H*-imidazol-1-yl)propan-1-amine (97%), chloroform, dichloromethane, potassium carbonate, calcium chloride, 1,4-dibromobutane (99%), 1,6-dibromohexane (96%), bromoacetyl bromide (98%), ethylene glycol (99%), 1,4-butanediol (99%), pyridine, and sodium bicarbonate were used. All chemicals and reagents were of analytical grade and were purchased from Merck and Sigma-Aldrich companies. The properties of the chemicals used in this study are presented in Table 1.

Article

2.2. Synthesis and Characterization. CGSs were synthesized according to Scheme 1. They were characterized





by FT-IR (Perkin Elmer 1600 FT-IR Spectrophotometer), mass spectroscopy (Bruker Microflex LT MALDI-TOF), and ¹H NMR and ¹³C NMR spectroscopy (Bruker AVANCE III 400 MHz Spectrometer).

2.2.1. Synthesis and Characterization of N-[3-(1H-Imidazol-1-yl)propyl] Dodecanamide. Dodecanoyl chloride (0.1 mol) was added slowly to the solution of 3-(1H-imidazol-1-yl)propan-1-amine (0.1 mol) in chloroform (100 mL), the solution was stirred under an inert atmosphere for 24 h at



Figure 1. ¹H NMR spectra of CGS4.

room temperature, and then the chloroform layer was extracted with saturated potassium carbonate solution, water, and brine.³⁶ The chloroform layer was dried with anhydrous calcium chloride. Also then, chloroform was removed under a decreased pressure. Last, the crude product was purified by crystallization by using acetonitrile/ethanol (95:5) as a solvent system.

FT-IR (KBr, ν/cm^{-1}): 3309 (NH), 2951–2914 (Aliph. C– H), 1643 (C=O), 1542 (C=N), 1511 (C=C). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 0.88 (bs, 3H, CH₃), 1.25 (bs, 16H), 1.61 (bs, 2H), 2.0 (m, 2H), 2.16 (t, 2H, *J* = 8.0 Hz), 3.26 (q, 2H), 4.00 (t, 2H, *J* = 8.0 Hz), 6.17 (s, NH), imid. H [6.95 (s, 1H), 7.05 (bs, 1H), 7.49 (s, 1H)]. ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 14.09, 22.65, 25.75, 29.32, 29.34, 29.48, 29.58, 29.60, 31.25, 31.88, 36.59, 36.67, 44.68, 118.92, 129.39, 137.05, 173.79 (C=O). MALDI-TOF-MS *m/z* calc. 307.47; found: 307.58 [M]⁺.

2.2.2. Synthesis and Characterization of Hydrophilic Spacers. Bromoacetyl bromide (0.2 mol) was added slowly to the solution of ethylene glycol (0.1 mol) or 1,4-butanediol (0.1 mol) in dichloromethane (50 mL), which also contained pyridine (0.2 mol) and DMAP (0.02 mol), and the solution was stirred under an inert atmosphere for 12 h at 273.15 K.³⁷ The resultant mixture was extracted with water, saturated sodium bicarbonate solution, and brine. Dichloromethane was removed under a decreased pressure. Brown oil crude products ethane-1,2-diyl bis(bromoacetate) and butane-1,4-diyl bis(bromoacetate) were obtained.

2.2.2.1. Ethane-1,2-diyl Bis(bromoacetate). FT-IR (KBr, ν/cm⁻¹): C–H; 2963, C=O; 1734, C–O–C; 1157; ¹H NMR (400 MHz, CDCl₃, δ /ppm): 3.83 (s, 4H, BrC<u>H₂</u>), 4.36 (s, 4H, $-OC\underline{H}_2C\underline{H}_2O-$); ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 25.50 (Br<u>C</u>H₂), 63.36 ($-O\underline{C}\underline{H}_2\underline{C}\underline{H}_2O-$), 167.02 (C=O). MALDI-TOF-MS *m*/*z* calc. 303.93; found: 303.39 [M]⁺.

2.2.2. Butane-1,4-diyl Bis(bromoacetate). FT-IR (KBr, ν/cm^{-1}): C–H; 2966, C=O; 1741, C–O–C; 1172; ¹H NMR (400 MHz, CDCl₃, δ /ppm): 1.77 (s, 4H, –CH₂–C<u>H₂–CH₂–</u> CH₂–), 3.84 (s, 4H, BrC<u>H₂</u>), 4.21 (s, 4H, O–C<u>H₂</u>); ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 24.98 (CH₂–<u>C</u>H₂–<u>C</u>H₂– CH₂), 25.79 (Br–CH₂), 65.65 (O–CH₂), 167.22 (C=O). MALDI-TOF-MS *m*/*z* calc. 331.99; found: 331.60 [M]⁺.

2.2.3. Synthesis and Characterization of CGSs (CGS1, CGS2, CGS3, and CGS4). N-[3-(1H-Imidazol-1-yl)propyl] dodecanamide (0.08 mol) and 1,4-dibromobutane (0.04 mol) or 1,6-dibromohexane (0.04 mol) or ethane-1,2-diyl bis(bromoacetate) (0.04 mol) or butane-1,4-diyl bis(bromoacetate) (0.04 mol) were mixed in a flask. The mixture was stirred at 333.15 K for 6 h under a nitrogen atmosphere. This product was washed and purified three times by recrystallization in heptane. CGSs with the same chain length and different spacers were obtained as a white powder.

2.2.3.1. 3,5⁷-Butane-1,4-diylbis{1-[3-(dodecanoylamino)propyl]-1H-imidazol-3-ium} Dibromide (CGS1). FT-IR (v_{max}, cm^{-1}) : N-H; 3308, C-H; 2954, 2919, C=O; 1650, C=N; 1539. ¹H NMR (DMSO- $d_6 \delta$ ppm): 0.85 (bs, 6H, CH₃, alkyl chain), 1.23 (bs, 32H, CH₂, alkyl chain), 1.47 (bs, 4H, O=C-CH₂C<u>H₂</u>), 1.82 (s, 4H, ⁺N-CH₂C<u>H₂</u>, spacer), 1.94 (bs, 4H, NH-CH₂C<u>H₂</u>), 2.07 (t, 4H, O=C-C<u>H₂</u>, J = 8.0 Hz, alkyl chain), 3.02 (bs, 4H, NH-C<u>H₂</u>), 4.19 (bs, 4H, N-C<u>H₂</u>), 4.25 (bs, 4H, ⁺N-C<u>H₂</u>, spacer), 7.85 (s, 4H, imid. H; NH),



Figure 3. MALDI-TOF MS of CGS4.

8.01 (s, 2H, imid. H), 9.36 (s, 2H, imid. H). ¹³C NMR (DMSO- $d_6 \delta$ ppm): 14.41, 22.56, 25.72, 26.44, 29.18, 29.20, 29.29, 29.43, 29.47, 29.51, 30.04, 31.76, 35.46, 35.88, 47.14, 48.53, 122.90, 122.97, 136.76, 172.96. MALDI-TOF-MS m/z calc. 751.86; found: 751.70 [M-Br]⁺.

2.2.3.2. 3,3'-Hexane-1,6-diylbis{1-[3-(dodecanoylamino)propyl]-1H-imidazol-3-ium} Dibromide (CGS2). FT-IR (v_{max} , cm⁻¹): N–H; 3305, C–H; 2953, 2917, C=O; 1640, C=N; 1539. ¹H NMR (DMSO- $d_6 \delta$ ppm): 0.84 (bs, 6H, CH₃, alkyl chain), 1.22 (bs, 32H, CH₂, alkyl chain; 4H, ⁺NCH₂CH₂CH₂CH₂, spacer), 1.46 (bs, 4H, O=C-CH₂CH₂, alkyl chain), 1.81 (bs, 4H, ⁺N-CH₂CH₂, spacer), 1.94 (bs, 4H, NH-CH₂CH₂), 2.07 (t, 4H, O=C-CH₂, *J* = 8.0 Hz), 3.02 (bs, 4H, NH-CH₂), 4.20 (bs, 8H, ⁺N-CH₂; N-CH₂), 7.86 (s, 4H, imid. H; NH), 8.04 (s, 2H, imid. H), 9.38 (s, 2H, imid. H). ¹³C NMR (DMSO- $d_6 \delta$ ppm): 14.36, 22.56, 25.19, 25.73, 29.21, 29.33,

29.46, 29.50, 29.54, 30.05, 31.78, 35.45, 35.85, 47.08, 49.09, 122.89, 136.70, 172.88. MALDI-TOF-MS m/z calc. 779.92; found: 780.68 [M-Br]⁺.

2.2.3.3. 3,3'-{Ethane-1,2-diylbis[oxy(2-oxoethane-2,1diyl)]}bis{1-[3(dodecanoylamino) propyl]-1H-imidazol-3ium} Dibromide (CGS3). FT-IR (v_{max} cm⁻¹): N–H; 3313, C–H; 2953, 2920, C=O; 1739, 1647, C=N; 1544, C–O–C; 1226. ¹H NMR (CDCl₃ δ ppm): 0.87 (bs, 6H, CH₃, alkyl chain), 1.24 (bs, 32H, CH₂, alkyl chain), 1.59 (bs, 4H, O=C– CH₂CH₂, spacer), 2.15 (bs, 4H, NH–CH₂CH₂), 2.26 (bs, 4H, O=C–CH₂, alkyl chain), 3.22 (bs, 4H, NH–CH₂), 4.44 (d, 8H, ⁺NCH₂, spacer; N–CH₂), 5.60 (bs, 4H, O=C–OCH₂, spacer), 7.71 (bs, 2H, NH), 7.80 (s, 2H, imid. H), 7.97 (s, 2H, imid. H), 9.88 (s, 2H, imid. H). ¹³C NMR (DMSO-d₆, δ ppm): 14.29, 22.56, 25.73, 29.22, 29.35, 29.48, 29.51, 29.56, 30.22, 31.78, 35.49, 35.85, 47.33, 50.14, 63.76, 122.59, 124.27, 137.87, 167.19, 173.00. MALDI-TOF-MS *m*/*z* calc. 762.88; found: 762.34 [M-2Br + 2]⁺.

2.2.3.4. 3,3'-{Butane-1,4-diylbis[oxy(2-oxoethane-2,1diyl)]}bis{1-[3-(dodecanoylamino) propyl]-1H-imidazol-3ium} Dibromide (CGS4). FT-IR (v_{max} cm⁻¹): N–H; 3315, С-Н; 2953, 2920, С=О; 1739, 1648, С=N; 1544, С-О-С; 1226. ¹H NMR (DMSO- $d_6 \delta$ ppm): 0.85 (bs, 6H, CH₃, alkyl chain), 1.23 (bs, 32H, CH₂, alkyl chain), 1.48 (bs, 4H, O=C- CH_2CH_2 , alkyl chain), 1.70 (bs, 4H, $O=C-OCH_2CH_2$, spacer), 1.93 (bs, 4H, NH-CH₂CH₂), 2.08 (t, 4H, O=C- CH_2 , J = 8.0 Hz, alkyl chain), 3.04 (bs, 4H, NH- CH_2), 4.19 (bs, 4H, N-CH₂), 4.26 (bs, 4H, ⁺NCH₂, spacer), 5.31 (bs, 4H, O=C-OCH₂, spacer), 7.81 (bs, 2H, NH), 7.89 (s, 2H, imid. H), 8.00 (s, 2H, imid. H), 9.29 (s, 2H, imid. H). ¹³C NMR (DMSO-*d*₆, δ ppm): 14.41, 22.56, 24.95, 25.71, 29.19, 29.29, 29.42, 29.47, 29.51, 30.31, 31.76, 35.50, 35.86, 47.36, 50.06, 65.66, 122.67, 124.35, 137.88, 167.32, 172.94. MALDI-TOF-MS *m*/*z* calc. 867.94; found: 867.92 [M]⁺.

The ¹H NMR spectra, ¹³C NMR spectra, and MALDI-TOF MS of CGS4 are given in Figures 1–3, respectively.

2.3. Physicochemical Properties. 2.3.1. Specific Conductivity Measurements. 2.3.1.1. Determination of Krafft Temperature. Krafft temperatures of CGSs were determined by a specific conductivity method.³⁸ Aqueous solutions of surfactants (1 wt %) were prepared, and then these solutions were kept refrigerated at ~277.15 K for at least 48 h. At the end of this period, the hydrate surfactant crystals were precipitated. Then, hydrate surfactant crystals were taken out of the refrigerator, and after, the temperature of systems was increased gradually under constant stirring. Conductivity data of systems were measured with a WTW Terminal 740 conductometer (cell constant = 0.485 cm^{-1}). Krafft temperatures were taken as the temperature at which the conductivity vs temperature plots represented a sudden break. During the specific conductivity run, the temperature uncertainty was ±0.1 K.

2.3.1.2. Determination of Critical Micelle Concentration. The specific conductivity data of CGS solutions were measured with the WTW Terminal 740 conductometer (cell constant = 0.485 cm^{-1}). The stock solutions of CGSs were prepared in molar concentration units at room temperature. A known volume of stock CGS solution was added incrementally into the volumetric flask containing double distilled deionized water, and thus, dilute solutions in different concentrations were obtained. The specific conductivity measurements of these solutions were performed in a temperature-controlled Thermo Scientific thermostatic water bath. Measurements for

the prepared dilute solutions of CGS1, CGS2, and CGS3 were carried out separately at 293.15, 303.15, 313.15, and 233.15 K. For the dilute solutions of CGS4, measurements were carried out separately at 303.15, 313.15, and 233.15 K. Double distilled deionized water was used as a solvent, and the specific conductivity of double distilled water was measured as 1.65 μ S· cm⁻¹ at 293.15 K. The measurements were used to determine the cmc values and to calculate some thermodynamic parameters of the all systems. The cmc values were provided from the break point of the specific conductivity (μ S·cm⁻¹) surfactant concentration (mM) isotherms.³⁶ The uncertainties in the measured specific conductivity and cmc were $\pm 0.5 \ \mu$ S· cm⁻¹ and $\pm 1.2 \times 10^{-5}$ M, respectively. During the specific conductivity run, the temperature uncertainty was ± 0.1 K.

2.3.2. UV-Visible Measurements. The solubilization measurements for Sudan III were performed using a Perkin Elmer Lamda 25 UV-Visible spectrophotometer. Mixtures of the excess powdered Sudan III with different concentrations of CGS solutions (above cmc) were stirred at 303.15 K at 200 rpm for 24 h. The mixture was centrifuged at 6000 rpm to remove undissolved solutes. Afterward, solutions were filtered to remove unsolubilized Sudan III. The amount of solubilized Sudan III was identified by absorbance measurements performed at 508 nm. Calibration with dilute solutions of Sudan III dissolved in ethanol has presented gratifying Beer-Lambert plots. The filtered solution was diluted with ethanol in the dissolution experiment. With this dilution, the amount of water was reduced enough to allow direct use of the calibration plot. Molar solubilization ratios of CGSs were determined by using eq139

$$MSR = (S_{T} - S_{cmc})/(C_{T} - C_{cmc})$$
(1)

In this equation, $C_{\rm T}$ is a particular total CGS concentration, $S_{\rm T}$ is the total apparent solubility of Sudan III in the CGS solution at $C_{\rm T}$, and $C_{\rm cmc}$ is the cmc value of CGS. $S_{\rm cmc}$ can be taken as the water solubility (S) due to its small change up to the cmc of the surfactant.

2.4. Emulsification Power. To determine the emulsification power, 10 mL (0.1% by weight) of each of the different CGS solutions was individually placed into a 100 mL cylinder, and then 10 mL of paraffin oil was added at 303.15 K. The cylinder was shaken vigorously for 10 min and then settled. The time needed to separate 9 mL of pure CGS solution was recorded (average of three readings) and was taken as an indication of the emulsification power (emulsion stability) of each CGS.⁴⁰

3. RESULTS AND DISCUSSION

3.1. Krafft Temperature. $T_{\rm K}$ is an important feature of an ionic surfactant that is firmly connected to the surfactant molecular structure. Micelle formations are only seen in aqueous solution above $T_{\rm K}$. When the temperature is lower than $T_{\rm K}$, hydration heat energy and the crystal lattice energy will have an effect on the solubility of ionic surfactants. At higher temperatures than $T_{\rm K}$, solubility increases considerably because a hydrated surfactant crystal melts and generates micelles in solution.⁴¹ Figure 4</sup> shows that the conductivity values increase gradually at low temperatures due to the very limited solubility of CGSs. There is a sudden increase in conductivity values until the $T_{\rm K}$ point is reached.

When the $T_{\rm K}$ values obtained have been examined, it has been observed that they have risen as usual with a rise in the number of carbon atoms contained in both hydrophilic and



Figure 4. Plot of specific conductivity vs temperature for CGS1, CGS2, CGS3, and CGS4.

hydrophobic spacer groups. CGS1 and CGS2 have hydrophobic spacers, while CGS3 and CGS4 have hydrophilic spacers. $T_{\rm K}$ values of CGS1, CGS2, CGS3, and CGS4 have been determined as 288.45, 285.45, 284.35, and 300.65 K, respectively. Data have indicated that the addition of two methyl groups to hydrophilic spacers increases $T_{\rm K}$ by at least 16 K but $T_{\rm K}$ is weakly affected by the addition of two methyl groups in hydrophobic spacers. The length of the spacer has a major impact on $T_{\rm K}$ of CGSs with hydrophilic spacers in this article. This has indicated that the spacer nature shows a determinative impact on the micellization temperature for hydrophilic spacers containing ester groups. When CGS1 and CGS3 containing short spacer groups have been compared with each other, it has been determined that the $T_{\rm K}$ value of CGS3 is approximately 4 K higher than the $T_{\rm K}$ value of CGS1.

When the carbon number in the hydrophobic spacer group has been increased, the hydrophobicity of CGS has been increased (CGS3 to CGS4) and interactions between head groups and Br ions have been decreased because the coulomb forces between head groups have decreased. The occurrence of these situations at the same time has been balanced by the effects of each other. Therefore, the increase in the carbon number of hydrophobic spacer groups has caused a slight change in $T_{\rm K}$.

By increasing the spacer chain length of CGS3 to CGS4, molecules accumulate in bulk and the solubility decreases due to hydrogen bonds that decrease with increasing hydrophobicity. Therefore, the solubility of the surfactant decreases and hence the $T_{\rm K}$ value increases. Because the CGSs synthesized in this study exhibit lower $T_{\rm K}$ values than the other monomeric and gemini surfactants,^{42–46} these CGSs present an advantage and have a wide temperature scale in terms of usage and application.

3.2. Critical Micelle Concentration. The conductivity technique has been utilized to define the cmc values of the CGSs. They have been acquired from the intersection point of two straight lines in a plot of specific conductivity vs [concentration]. The specific conductivities vs concentrations of CGSs at different temperatures are presented in Figures 5–8. Because the $T_{\rm K}$ value for CGS4 is 300.65 K, we have not carried out specific conductivity studies at 293.15 K. The cmc values are considerably lower than conventional surfactants such as tetradecyltrimethylammonium bromide and dodecyl-trimethylammonium bromide at the same temperature.^{47,48} Additionally, cmc data for these novel CGSs are lower than



Figure 5. Plot of specific conductivity vs concentration at different temperatures for CGS1.



Figure 6. Plot of specific conductivity vs concentration at different temperatures for CGS2.



Figure 7. Plot of specific conductivity vs concentration at different temperatures for CGS3.



Figure 8. Plot of specific conductivity vs concentration at different temperatures for CGS4.

those for other nonfunctionalized and functionalized imidazolium surfactant types.^{19,34,49,50} This behavior is likely because of the multiple amide bonds in their chemical structure.⁵¹

In this study, cmc values of CGSs have been determined to be close to each other; however, the highest cmc value has been provided at 303.15 K when the lowest number of carbon atom of hydrophobic spacer (CGS2) has been incorporated in the imidazolium-based cationic gemini surfactant structure. The lowest cmc data has been measured in the CGS with the lowest number of carbon atoms in hydrophobic spacer, namely, CGS1. The cmc values are effected from two basic factors. The first of these factors is the electrostatic repulsion because of a similar charge in head groups. The second of these factors is the hydrophobic interactions among the hydrocarbon tails in both components. All CGSs studied for this paper contain positive charges similar to each other on their head groups. Therefore, the repulsion among the head groups leads to restrictions on the formation of the micelle. The increased hydrophobic interactions are more effective than these restrictions and improve the formation of the micelle.

The impact of temperature on cmc in ionic surfactants essentially has two perspectives. Increasing temperature decreases the degree of hydration in hydrophilic head groups. This provides an advantage in micelle formation and reduces cmc. Conversely, the sequential structure of water molecules around the hydrocarbon chain may be broken so as to support solubility of surfactant monomers and prevent the micellization of surfactant monomers.⁵² The values of cmc generally have been increased by increasing temperatures for all CGSs in this study.

Additionally, thermodynamic parameters for micellization have been determined with specific conductivity measurement data. Conductivity data show a continued increase by rising temperature. This is likely due to an increase in the thermal energy in the systems. The cmc value for an amphiphile at a given temperature is controlled by the van der Waals interaction between hydrophobic parts that tend to form micelles, while hydration of head groups tends to delay micelle formation.⁵³ From a thermodynamic point of view, a highly charged surface is unstable because electrostatic repulsion causes the surface energy to increase. Thus, the combination of ionic micelles with counterions slightly neutralizes the surface charge and minimizes electrostatic repulsion. In specific conductivity concentration profiles, two linear segments have been observed, one above and below the cmc. The low slope of the second slope means that the micelles formed have less mobility than free ions in solution.⁵⁴

Furthermore, degrees of counterion dissociation (α) data have been provided from the ratio of the slopes above and below the cmc ($\alpha = \text{slope}_2/\text{slope}_1$).⁵⁵ The difference in the degree of counterion dissociation (α) data is because of the difference in the shape of the micelles. Also then, the degree of

Table 2	2. cmc, α, þ	, and S	Some T	Thermodynami	c Parameters	of	CGSs	at	Different	Temperatures"	ľ
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cmc (M)	α	β	$\Delta G_{ m mic}^{ m o}~({ m kJ}{ m \cdot mol}^{-1})$	$\Delta H_{ m mic}^{ m o}~({ m kJ}{ m \cdot}{ m mol}^{-1})$	$-T\Delta S_{ m mic}^{ m o}$ (kJ·mol ⁻¹)
4.59×10^{-4}	0.378	0.622	-63.99	-13.30	50.69
4.71×10^{-4}	0.399	0.601	-64.79	-13.96	50.83
5.00×10^{-4}	0.417	0.584	-65.54	-14.66	50.87
5.92×10^{-4}	0.423	0.577	-66.24	-15.52	50.72
5.12×10^{-4}	0.427	0.573	-60.62	-9.04	51.58
5.74×10^{-4}	0.447	0.553	-60.94	-9.49	51.45
5.84×10^{-4}	0.471	0.530	-61.45	-9.90	51.54
6.19×10^{-4}	0.480	0.520	-62.50	-10.45	52.05
4.95×10^{-4}	0.569	0.431	-52.79	-9.71	43.07
5.00×10^{-4}	0.574	0.426	-54.21	-10.33	43.88
5.10×10^{-4}	0.579	0.421	-55.62	-10.96	44.66
5.14×10^{-4}	0.580	0.420	-57.30	-11.66	45.64
4.89×10^{-4}	0.439	0.561	-62.27	-26.92	35.35
5.86×10^{-4}	0.461	0.539	-62.01	-28.13	33.88
6.81×10^{-4}	0.467	0.533	-62.78	-29.78	33.00
	cmc (M) 4.59×10^{-4} 4.71×10^{-4} 5.00×10^{-4} 5.92×10^{-4} 5.12×10^{-4} 5.74×10^{-4} 5.84×10^{-4} 6.19×10^{-4} 4.95×10^{-4} 5.10×10^{-4} 5.14×10^{-4} 4.89×10^{-4} 5.86×10^{-4} 6.81×10^{-4}	cmc (M) α 4.59×10^{-4} 0.378 4.71×10^{-4} 0.399 5.00×10^{-4} 0.417 5.92×10^{-4} 0.423 5.12×10^{-4} 0.427 5.74×10^{-4} 0.447 5.84×10^{-4} 0.471 6.19×10^{-4} 0.480 4.95×10^{-4} 0.569 5.00×10^{-4} 0.574 5.14×10^{-4} 0.579 5.14×10^{-4} 0.580 4.89×10^{-4} 0.439 5.86×10^{-4} 0.461 6.81×10^{-4} 0.467	cmc (M) α β 4.59 × 10 ⁻⁴ 0.3780.6224.71 × 10 ⁻⁴ 0.3990.6015.00 × 10 ⁻⁴ 0.4170.5845.92 × 10 ⁻⁴ 0.4230.5775.12 × 10 ⁻⁴ 0.4270.5735.74 × 10 ⁻⁴ 0.4470.5535.84 × 10 ⁻⁴ 0.4710.5306.19 × 10 ⁻⁴ 0.4800.5204.95 × 10 ⁻⁴ 0.5740.4265.10 × 10 ⁻⁴ 0.5790.4215.14 × 10 ⁻⁴ 0.5790.4215.14 × 10 ⁻⁴ 0.5800.4204.89 × 10 ⁻⁴ 0.4390.5615.86 × 10 ⁻⁴ 0.4610.5396.81 × 10 ⁻⁴ 0.4670.533	cmc (M) α β ΔG_{mic}° (kJ·mol ⁻¹) 4.59×10^{-4} 0.3780.622-63.99 4.71×10^{-4} 0.3990.601-64.79 5.00×10^{-4} 0.4170.584-65.54 5.92×10^{-4} 0.4230.577-66.24 5.12×10^{-4} 0.4270.573-60.62 5.74×10^{-4} 0.4470.553-60.94 5.84×10^{-4} 0.4710.530-61.45 6.19×10^{-4} 0.4800.520-62.50 4.95×10^{-4} 0.5690.431-52.79 5.00×10^{-4} 0.5740.426-54.21 5.10×10^{-4} 0.5790.421-55.62 5.14×10^{-4} 0.5800.420-57.30 4.89×10^{-4} 0.4390.561-62.27 5.86×10^{-4} 0.4610.539-62.01 6.81×10^{-4} 0.4670.533-62.78	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^{*a*}The standard uncertainties (*U*) are *U* (cmc): $1.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, *U* (α): 0.002, *U* (β): 0.002, *U* ($\Delta G^{\circ}_{\text{mic}}$): 0.2 kJ·mol⁻¹, *U* ($\Delta G^{\circ}_{\text{mic}}$): 0.2

counterion binding values to the micelles (β) have been determined with equation $\beta = (1 - \alpha)$. Understanding the specific binding of counterions to micelles is a prerequisite for understanding both micellization and any aggregation in aqueous solutions. Therefore, many discussions have focused on the degree of counterion binding to micelles.³⁴ β gives the ability of counterions to bind micelles in the Stern layer. It is observed that β values have decreased with increasing alkyl spacer length for the studied CGSs that have hydrophobic spacers. The two head groups are closely spaced because the CGS has a shorter spacer length. Consequently, the charge density increases and simplifies higher counterion binding. β values of CGS decrease with increasing temperature. Hence, it can be suggested that counterions bind to the micelle surface through an exothermic process.⁵⁶ The cmc values of CGSs are shown in Table 2. When the data in Table 2 are analyzed, it is observed that the values of β decrease as the temperature increases because the thermal motion of surfactant aggregates is condensed with increasing temperature.⁵

The standard $\Delta G_{\text{mic}}^{\circ} \Delta H_{\text{mic}}^{\circ}$ and $\Delta S_{\text{mic}}^{\circ}$ of micellization have been calculated with the following equations:⁵⁸

$$\Delta G_{\rm mic} = RT(3 - 2\alpha) \ln X_{\rm cmc} \tag{2}$$

$$\Delta H_{\rm mic} = -RT^2 \left[(3 - 2\alpha) \left(\frac{\partial \ln X_{\rm cmc}}{\partial T} \right)_{\rm p} - \ln X_{\rm cmc} \left(\frac{\partial \alpha}{\partial T} \right)_{\rm p} \right]$$
(3)

$$\Delta S_{\rm mic} = \frac{\Delta H_{\rm mic} - \Delta G_{\rm mic}}{T} \tag{4}$$

In these equations, $X_{\rm cmc}$ is the mole fraction of CGS in aqueous solution at cmc and $n_{\rm cmc}/n_{\rm cmc} + n_{\rm water}$ and $n_{\rm water}$ are the moles of CGS and water, respectively. α is the degree of counterion dissociation, R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), and T is the temperature (K).

 $\Delta G_{\rm mic}^{\rm o}$, $\Delta H_{\rm mic}^{\rm o}$, and $\Delta S_{\rm mic}^{\rm o}$ of CGS at 293.15, 303.15, 313.15, and 323.15 K are presented in Table 2. CGS4 cannot be calculated at 293.15 K due to the solubility limit of this surfactant at this temperature. $\Delta G_{\rm mic}^{\rm o}$ has been found to be negative for CGSs under investigation. It is usually inversely proportional to temperature. It has been observed in Table 2 that $\Delta G_{\rm mic}^{\rm o}$ has been closely related to the nature of spacer, where CGS1 has the smallest values. The values of $\Delta G_{\rm mic}^{\rm o}$ for CGS1, CGS2, CGS3, and CGS4 in this study are -64.79, -60.94, -54.21, and -62.27 kJ·mol⁻¹ at 303.15 K, respectively. These negative $\Delta G_{\rm mic}^{\rm o}$ values rise in magnitude with the increased temperature of all CGSs. The results indicated that thermodynamically stable micelles form spontaneously and the more negative value of $\Delta G_{\rm mic}^{\rm o}$ means more stable surfactant micelles.

The values for $\Delta H_{\rm mic}^{o}$ are also negative. These negative values indicate that the micelle formation is an exothermic process and reduces with the increase in temperature of all studied gemini surfactants. This indicates that the changes in the temperature affect the environment around the hydrophobic chain of CGS molecules. It has been seemingly indicated that $|-T\Delta S_{\rm mic}^{o}|$ has been a much larger value than $\Delta H_{\rm mic}^{o}$ under all studied conditions, showing that entropy has been the driving force in the micellization processes. Obviously, the main contribution to $\Delta G_{\rm mic}^{o}$ during micelle formation came from the value of $\Delta S_{\rm mic}^{o}$. For this reason, the micellization process of CGS has been an entropy-based process over the temperature range studied. Positive $\Delta S_{\rm mic}^{\circ}$ values showed that the process of forming micelles would increase the degree of disorder of the system. As seen from Table 2, $|-T\Delta S_{\rm mic}^{\circ}|$ values have generally increased with increased temperature. Namely, molecular action of surfactants has been increased by temperature. Therefore, the rise in temperature has increased chaos in the system.⁵⁹

3.3. Solubilization. In many industrial processes, it is important to dissolve the materials insoluble in water in the surfactant aqueous solution.⁶⁰ The solubilization of Sudan III, an organic dye, has been investigated in the different concentrations of CGS by UV–Vis spectroscopy in this paper. In the case of Sudan III, with the increase in surfactant concentration, the amount of dye solubilized in micelles also increased in all the CGSs studied (Figure 9). It can be



Figure 9. Plot of $S_{\rm T}$ vs $(C_{\rm T} - C_{\rm cmc})$ for CGS1, CGS2, CGS3, and CGS4.

confirmed that the slope of the linear plots means the molar solubilization ratio, MSR, which presents the amount of dye solubilized per mol of micellar surfactant. MSR has increased in the order of CGS4 < CGS1 < CGS3 < CGS2. The MSR values of CGS1, CGS2, CGS3, and CGS4 have been found to be 0.4999, 1.2765, 0.7164, and 0.4289, respectively.

The MSR value of the Sudan III dye in the micelles formed by CGS2 with the hydrophobic spacer group of six carbon atoms was bigger than the other studied CGS1, CGS3, and CGS4. The higher MSR value of Sudan III in the CGS2 solution systems as compared to the others may be due to the volume of the micelles for effective solubilization. The MSR value of the Sudan III dye in the micelles formed by CGS3 with the short hydrophilic spacer group has been determined to be higher than those by CGS2 and CGS4. This may be related to polar ester bonds in CGS3. It could be due to the hydrogen bonds and ion—dipole interactions between Sudan III and CGS3. MSR values of studied CGS have been found to be higher than those of the other monomeric and gemini surfactants.

3.4. Emulsification Power. The emulsification power in functional chemicals is an important parameter due to the requirement for any chemical in the oilfield application region to be compatible with crude oil without increasing its emulsification in water.⁶¹ The time taken for the breakdown of the emulsion formed among paraffin oil and surfactant solution determines the emulsification power for CGSs (Figure

10). Obviously, the emulsification power in CGSs depends entirely on the nature of the spacer. CGS3, which contains a



hydrophilic short spacer, has the lowest emulsification tendency (961 s).

The emulsification power has significantly increased with increasing hydrophilic spacer chain length (CGS4, 1652 s). Increasing hydrophobicity in molecules with the gradual increase of $-CH_2-CH_2-$ groups in the hydrophilic spacer increases their tendency to migrate from the aqueous medium to the oil medium and accordingly increases their emulsification power. The greater the hydrophobic property of the molecules, the greater the stability of the oil-in-water emulsion formed.^{62,63} The emulsification power of CGS1 (2722 s) has been found to be the best of the series studied. Additionally, the emulsification power of CGS2 has been found as 2412 s. We determined that CGS1 and CGS2, which have hydrophobic spacers, show higher emulsification power than CGS3 and CGS4, which have hydrophilic spacers.

4. CONCLUSIONS

A new series of CGSs have been synthesized and characterized, and their micellar properties at different temperatures have been investigated. Results indicated that the $T_{\rm K}$ value (especially CGSs with hydrophilic spacers) has been affected by the nature of spacers. Since the CGSs studied in this article show lower T_K values than conventional surfactants commonly used, we can say that these CGSs have excellent application potential at low temperatures. These new series of CGSs have represented very low cmc. These substances can be used with conventional surfactants in occurring binary mixtures to create superior surface properties. Cationic gemini surfactants in this study can be used as emulsifying agents (especially CGSs with hydrophobic spacers) since the results of the emulsion stability measurements are satisfactory. These surfactants can be used for the enhanced solubilization of hydrophobic materials such as dyes, drugs, or pesticides. This work provides fundamental information about interfacial and micellar properties of gemini surfactants and assists new applications in industrial and academic areas.

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Notes

The authors declare no competing financial interest.

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