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Synthesis and Physicochemical Properties of Double-Chain Cationic Surfactants

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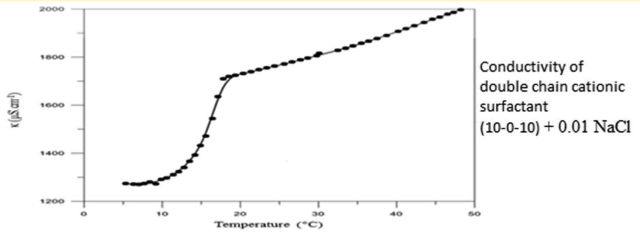
Supporting Information

ABSTRACT: In this study two types cationic surfactants were synthesized, purified, and characterized in our laboratory. One them is a series of cationic surfactants, a two tail−one head surfactant, *N*,*N*-dialkyl-*N*,*N*-diethylammonium bromide, abbreviated as "*m*-0-*m*" ($m = 10$, 12, and 16). The other type is *N*,*N*′-dialkyl-*N*,*N*,*N*′,*N*′-tetramethyl-*N*,*N*′-ethanediyl-diammonium dibromide, two tail−two head surfactants, abbreviated as "*m*-2-*m*" ($m = 12$ and 16). Once NMR spectra (^{1}H NMR, ^{13}C NMR) for all the gemini surfactants that were synthesized were taken, then the melting temperatures (T_M) were measured. These surfactants have very high surface activity. The main goal of our study was to examine some properties of these two tail cationic surfactants by manipulating their dimeric structure. The effects of alkyl chain length and headgroup on surfactant self-assembly in solution were investigated. Critical micelle concentrations (CMC), degree of micelle ionization (α), and Krafft temperatures (T_K) of 1 wt % aqueous solutions of these surfactants were determined by conductance measurements. Krafft points were found to be dependent on the number of carbon atoms in the alkyl chain and decreased by the addition of the electrolytes. The absence of the spacer group, peculiar to these twin tail cationic surfactants, may confer relatively low flexibility to the molecules, with potential implications on the interfacial properties, namely, on micellization.



1. INTRODUCTION

Surfactants are amphiphilic molecules that when dissolved in water or an aqueous solution act as surface tension reducing substances. Conventional or meric surfactants normally contain both one water-soluble (hydrophilic) group and one oil soluble (hyrophobic) group and are widely used in industrial processes.[1,2] Chemists have been in search of newer surfactants which have great surface activity, and they started with bis-surfactants, which were later renamed as "Gemini surfactants". Menger and Littau[3] assigned the name Gemini to bis-surfactants with a rigid spacer. Gemini or dimeric surfactants have amphiphiles composed of two hydrophobic chains and two hydrophilic headgroups linked by a spacer group that can be hydrophobic/hydrophilic and flexible/rigid.[4,5] Dimeric surfactants showed two important features with respect to the meric surfactants: High efficiency to reduce the surface tension of water and much lower CMC values (10 to 100 times lower than corresponding meric surfactant).[6,7] The Geminis are extensively investigated for their possible use in formulations. The alkanediyl-α,ω-bis(alkyldimetyl ammonium bromide) types have been the most investigated dimeric surfactants.[8−10] They are often abbreviated as *m*-*s*-*m* surfactants, where *m* and *s* are the numbers of carbon atoms in the side alkyl chain and the spacer, respectively. The great majority of Geminis are basically dimeric homologues of monomeric surfactants.[11] The various micellar properties of Gemini surfactants and their mixtures, such as critical micelle concentrations, degree of micelle ionization, aggregation number of their micelles, thermodynamics of micelle formation, micropolarity, microviscosity, and other interfacial properties, have been examined by different techniques,[12−17] reported, and discussed. Some unsymmetrical Geminis and Geminis with three or more polar groups or tail have recently been reported.[18,19] Our current focus of interest is a new generation of cationic surfactant, which would have better properties and unique characteristics in the adsorption micellization process. In this study, the novel surfactants with two hydrocarbon chains attached to one headgroup have been synthesized, purified, and characterized in our laboratory. To our knowledge, no research has investigated the features of our newly synthesized compounds. There are a few studies for double-chain cationic surfactants from the class of *N*,*N*-dialkyl-*N*,*N*-dimethylammonium bromide surfactants.[20,21] Bakshi et al. had used twin tail alkylammonium cationic surfactants 12-6-12 and 12-0-12 as capping agents for synthesis of gold nanoparticles, but that possessed an alkyl with a 12 carbon (our products have an alkyl with 10, 12, and 16 carbons and ethyl substitution is used instead of methyl substitution).[22] The ethyl substitution is the novelty in the synthesized structures.

Ionic surfactants can be precipitated from aqueous solutions as solid hydrates. This is an important characteristic feature for

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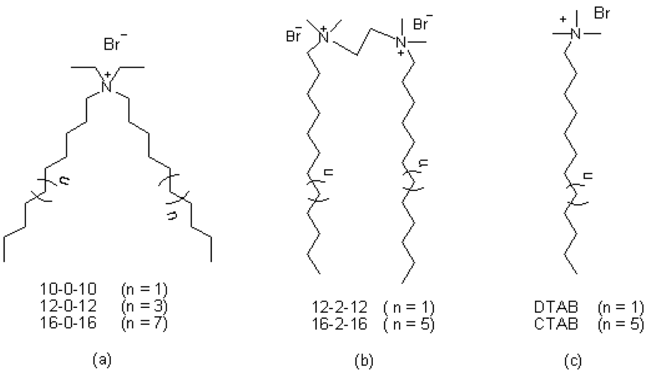
ionics. Before the critical micelle concentration, ionic surfactants become insoluble in solution. The solubilities of micelle forming surfactants show a strong increase above a certain temperature, termed as Krafft temperature, T_K (also known as Krafft point or critical micelle temperature).[23] Below T_K, the solubility of the surfactant is too low for micellization; therefore, solubility alone determines the surfactant monomer concentration. Above T_K a relatively large amount of surfactant can be dispersed in micelles, and solubility increases greatly. A surfactant with a low Krafft point is more soluble than a surfactant with a high Krafft point.

In this study, a series of *N*,*N*-dialkyl-*N*,*N*-diethyl ammonium bromide, two tail−one head surfactants, abbreviated as "*m*-0-*m*" (*m* = 10, 12, and 16) and *N*,*N*′-dialkyl-*N*,*N*,*N*′,*N*′-tetramethyl-*N*,*N*′-ethanediyl-diammonium dibromide, two tail−two head surfactants, abbreviated as "*m*-2-*m*" (*m* = 12 and 16) were synthesized in our laboratory. Critical micelle concentrations (CMCs), degree of micelle ionization (α), Krafft temperatures (T_K) of 1 wt % aqueous solutions of these surfactants, and melting points (T_M) were determined. The Krafft temperatures of some monomeric, dimeric, and double chain cationic surfactants have been systematically investigated by using a conductometer. The effects of the hydrophobic alkyl chain, headgroup, and spacer on cationic surfactants are explained by using the CMC and T_K values which were found for the studied surfactants. In addition, the effects of NaCl molality on the Krafft temperature of various cationic surfactants have been examined.

2. EXPERIMENTAL SECTION

2.1. Materials. Hexadecyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) cationic surfactants were obtained from Merck. *N*,*N*′ didodecyl-*N*,*N*,*N*′,*N*′-tetramethyl-*N*,*N*′-ethanediyldiammonium dibromide (12-2-12), *N*,*N*-hexadecyl-*N*,*N*,*N*′,*N*′-tetrametyl-*N*,*N*′-ethanediyldiammonium dibromide (16-2-16) Gemini cationic surfactants and *N*,*N*-didecyl-*N*,*N*-diethylammonium bromide (10-0-10), *N*,*N*-didodecyl-*N*,*N*-diethylammonium bromide (12-0-12), and *N*,*N*-dihexadecyl-*N*,*N*-diethylammonium bromide (16-0-16) double chain cationic surfactants have been synthesized and purified in our laboratory. Structures of surfactant molecules used in this study are given in Scheme 1, and ^{1}H and ^{13}C NMR spectra of surfactants were recorded with Varian Mercury Plus 300 MHz spectrometer (see Supporting Information). The chemicals as well as their purities and suppliers are listed in Table 1.

Scheme 1. Structures of Surfactant Molecules Used in This Study: (a) Double-Chain Cationic Surfactants, (b) Gemini Surfactants, and (c) Conventional Surfactants



Synthesis of Cationic Gemini Surfactants. Cationic Gemini surfactants used in this work were synthesized as described by Zana et al.[24] and are shown in Scheme 2. Acetone is used as solvent.[25] The reaction products were obtained in yields of about 90−97%, and these products were purified and recrystallized.

Spectral Characteristics for 12-2-12. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 6H), 1.17−1.30 (m, 36H), 1.81 (m, 4H), 3.47 (s, 12H), 3.70 (m, 4H), 4.70 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.38, 22.92, 23.28, 26.48, 29.42, 29.60, 29.77, 29.80, 29.88, 32.15, 51.30, 57.02, 66.09.

Spectral Characteristics for 16-2-16. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 6H), 1.23−1.34 (m, 52H), 1.82 (m, 4H), 3.46 (s, 12H), 3.70 (m, 4H), 4.69 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.38, 22.93, 23.27, 26.47, 28.40, 29.00, 29.43, 29.60, 29.62, 29.67, 29.79, 29.83, 29.92, 29.98, 32.16, 51.26, 57.07, 66.02.

Synthesis of Double-Chain Cationic Surfactants. The double chain cationic surfactants didecyldiethylammonium bromide, didodecyldiethylammonium bromide, and dihexadecyldiethylammonium bromide synthesized from diethyl amine and corresponding alkyl halide by two-stage reaction are shown in Schemes 3 and 4.

To a solution of diethylamine (0.2 mol) in dry acetone was added alkyl halide (0.1 mol), and the solution was stirred for 6 h at reflux temperature. Then, the reaction mixture was cooled to room temperature and was quenched with 1% KOH solution. The aqueous layer was extracted with diethyl ether three times and was washed in brine solution. The organic layers were collected and dried over anhydrous Mg_2SO_4 (Scheme 3).

In the next stage, reaction of diethylalkylamine with the same alkyl halide in acetone gave dialkyldiethylammonium bromide (Scheme 4).

Spectral Characteristics for 10-0-10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 6H), 1.20−1.70 (m, 38H), 3.20−3.30 (t, 4H), 3.50−3.60 (quartet, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.40, 14.30, 22.40, 22.90, 26.70, 29.40, 29.50, 29.60, 32.00, 54.40, 58.40.

Spectral Characteristics for 12-0-12. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H), 1.20−1.80 (m, 46H), 3.20−3.30 (t, 4H), 3.50−3.60 (quartet, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.40, 14.30, 22.30, 22.90, 26.70, 29.40 29.50, 29.60, 29.70, 29.80, 32.10, 54.40, 58.30.

Spectral Characteristics for 16-0-16. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H), 1.20−1.70 (m, 62H), 3.20−3.30 (t, 4H), 3.50−3.60 (quartet, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.40, 14.40, 22.30, 22.90, 26.70, 29.40 29.60, 29.62, 29.70, 29.82, 29.89, 29.92, 32.20, 54.37, 58.27.

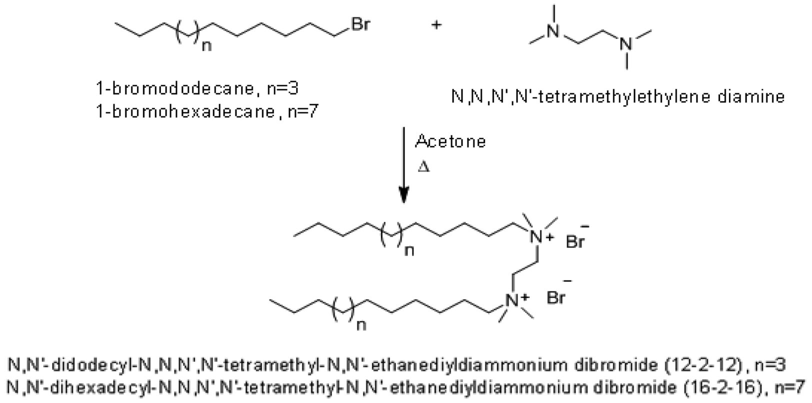
2.2. Apparatus and Procedure. *Conductivity Measurements.* The conductivity measurements of surfactant solutions were taken with a conductometer WTW Terminal 740 using a dip-type cell with a cell constant of 0.485 cm^{-1}. Equipment was initially calibrated by standard KCl solutions. Conductivity values were for to find three different physicochemical characteristics: critical micelle concentration (CMC), degree of micelle ionization (α), and Krafft temperatures (T_K). Deionized double distilled water was used in all experimental work, and its specific conductivity value was about $1{-}2 \times 10^{-6}$ S cm^{-1}. All the experimental data were taken at 30.0 ± 0.1 °C.

Table 1. Specification of Chemical Samples

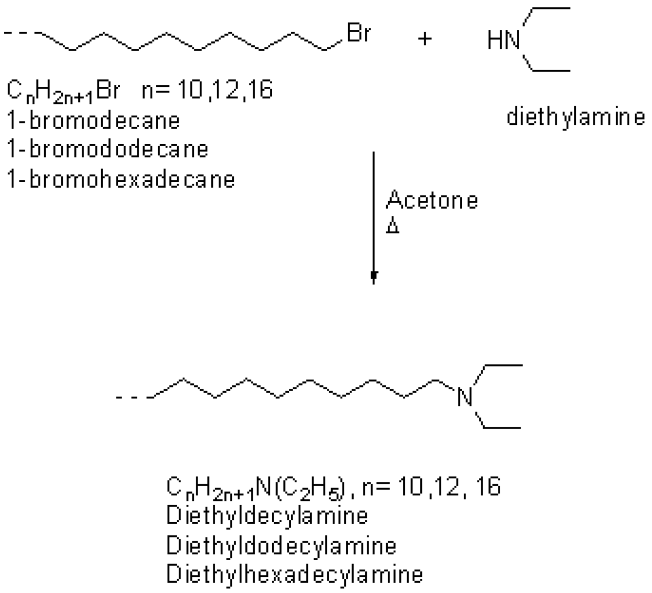
chemical name	source	initial mass fraction purity	purification method	final mole fraction purity	analysis method
dodecyltrimethylammonium bromide (DTAB)	Merck	99%	none	-	-
cetyltrimethylammonium bromide (CTAB)	Merck	99%	none	-	-
1-bromodecane	Fluka	≥97%	none	-	-
1-bromododecane	Fluka	≥95%	none	-	-
1-bromohexadecane	Fluka	≥97%	none	-	-
N,N,N′,N′-tetramethylethylene diamine	Fluka	≥98%	none	-	-
diethylamine	Merck	>99%	None	-	-
N,N′-didodecyl-*N,N,N′,N′*-tetramethyl-*N,N′*-ethanediyldiammonium dibromide (12-2-12)	-	synthesis	recrystallization	97%	^{13}C NMR[a] ^{1}H NMR[b]
N,N-hexadecyl-*N,N,N′,N′*-tetrametyl-*N,N′*-ethanediyldiammonium dibromide (16-2-16)	-	synthesis	recrystallization	98.5%	^{13}C NMR[a] ^{1}H NMR[b]
N,N-didecyl-N,N-diethylammonium bromide (10-0-10)	-	synthesis	recrystallization	≥99.5%	^{13}C NMR[a] ^{1}H NMR[b]
N,N-didodecyl-*N,N*-diethylammonium bromide (12-0-12)	-	synthesis	recrystallization	≥99.5%	^{13}C NMR[a] ^{1}H NMR[b]
N,N-dihexadecyl-*N,N*-diethylammonium bromide (16-0-16)	-	synthesis	recrystallization	≥99.5%	^{13}C NMR[a] ^{1}H NMR[b]

[a] ^{13}C nuclear magnetic resonance spectroscopy. [b] ^{1}H nuclear magnetic resonance spectroscopy.

Scheme 2. Synthesis of *m*-2-*m* Type Cationic Gemini Surfactants



Scheme 3. Synthesis of Diethylalkylamines



Critical Micelle Concentration (CMC) Measurements. The CMC is an important physiochemical property for characterizing the self-aggregation of a surfactant in a solution. First, different surfactant solutions were prepared in water, and their concentrations were at least 10 times higher than CMC of surfactants. CMC values were found from the conductivity plotted against the concentration of surfactant.

Degree of Micelle Ionization (α). Also, electrical conductivity values were used for determination of the degree of micelle ionization ($\alpha = S_2/S_1$), where S_1 and S_2 are the slopes below and above the CMC in the curve of specific conductivity against surfactant concentration.[26] The premicellar slope was always higher than the post micellar slope, and their ratios were used for the evaluation of the values of degree of micelle ionization. All the values obtained this method are listed in Table 2.

Krafft Temperature Measurements. In ionic surfactant solutions, the solubility of the surfactant increases dramatically after a certain temperature. This temperature is named as the Krafft point (T_K) which at this temperature micellization starts for ionic surfactant. For Krafft temperature measurements, first, the fixed surfactant solutions of 1 wt % were prepared in pure water and in the presence of the NaCl.[27] Second, the prepared

Scheme 4. Synthesis of Dialkyldiethylammonium Bromide Compounds

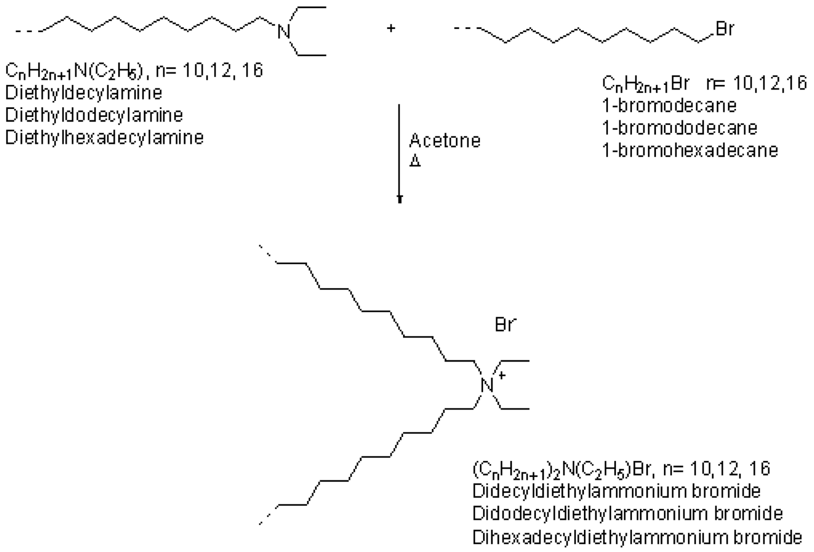


Table 2. Values of Critical Micelle Concentrations (CMC)[a], Degree of Micelle Ionization (α), and the Degree of Binding Counterion of Studied Surfactants at 30.0 °C and 0.1 MPa

surfactant	CMC m/(mol kg^{-1})	degree of ionization (α)	degree of binding counterion (β)
double-chain cationic (10-0-10)	1.00×10^{-3}	0.06	0.94
double-chain cationic (12-0-12)	1.02×10^{-4}	0.11	0.89
double-chain cationic (16-0-16)	1.50×10^{-5}	0.12	0.88
cationic Gemini (12-2-12)	9.60×10^{-4}	0.19	0.81
cationic Gemini (16-2-16)	3.30×10^{-5}	0.18	0.82
cationic DTAB	1.50×10^{-2}	0.31	0.69
cationic CTAB	9.50×10^{-4}	0.32	0.68

[a] Standard uncertainties for molality, u(m) are 1x 10^{-6} mol.kg^{-1} for Geminis and 1x 10^{-5} mol.kg^{-1}for conventional surfactants. Standard uncertainties u (t) in temperatures are 0.1 °C and Standard uncertainties in u (p) are 0.01 MPa.

solutions have been kept refrigerated for the realization for at least 1 day at a temperature of approximately 3.5 °C. Under this condition, the precipitation of the hydrated surfactant occurs. In some conditions, the solution had to be frozen and then left to melt slowly at about 1.5 °C to obtain a precipitate for the studied surfactant. Then, the systems were taken out the refrigerator and then the temperature of the precipitated systems was raised gradually under constant stirring. The electrical conductivities of solutions were measured using a WTW Terminal 740 (cell constant = 0.485 cm^{-1}) conductometer by increasing the temperature by increments of 0.1 °C. The Krafft temperature was taken as the temperature where the conductance, $\mathcal{K}$, vs temperature plots showed a break.[28,29] The Krafft temperatures of all pure cationic surfactants were determined in this way, and only two of them, Gemini 12-2-12 and double-chain cationic surfactants 12-0-12, are shown in Figures 1 and 2. Also, Krafft temperatures for all cationic surfactants are summarized in Table 2. The Krafft temperature listed below 0 °C gave no precipitate when kept in ice water for at least 24 h. The effects of electrolyte molalities on Krafft temperature in a 1 wt % solution of surfactants were determined in the same way.

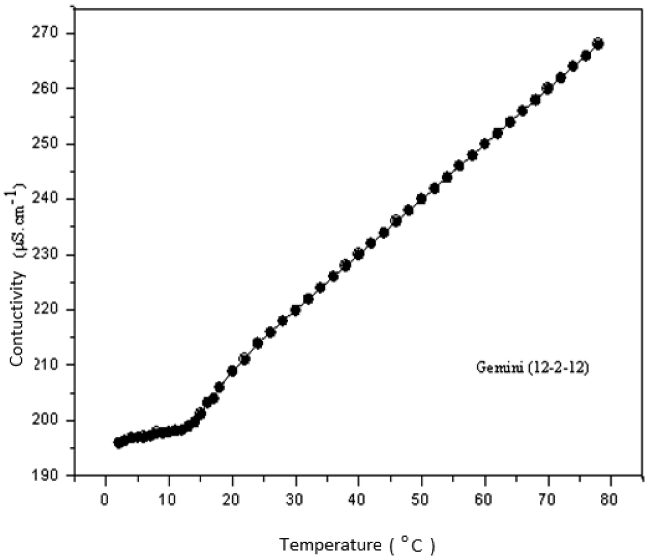


Figure 1. Temperature dependence of conductivity in Gemini 12-2-12 solution at 0.1 MPa.

Melting Point Measurements. The melting points of all studied cationic surfactants (T_M) were measured using a Gallenkamp 5a 6797 melting point instrument. The equipment has a sensitive platinum resistance thermometer which is capable of rapid response to temperature changes, so that measurements give the most accurate values with resolution of 0.5 °C. The samples of all surfactants were prepared in thin glass-capillary tubes, closed in one end. The capillary tube was placed in the instrument. While the temperature was gradually increased, the melting event is observed. Samples were dried over phosphorus pentaoksit prior to measurements. Measurement was repeated at least three times, and results were expressed as average of measured values.

3. RESULTS AND DISCUSSION

3.1. CMC and Degree of Micelle Ionization. Figure 3 shows the specific conductivity, κ, versus concentration plots

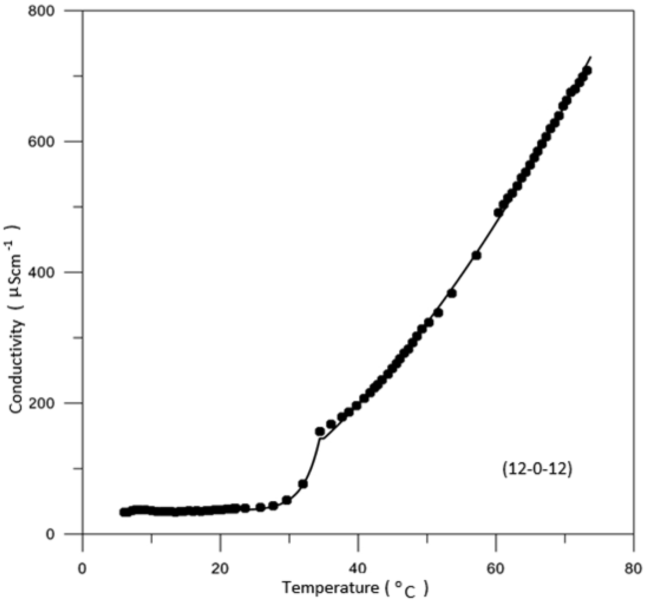


Figure 2. Temperature dependence of the conductivity in double-chain cationic surfactant 12-0-12 solution at 0.1 MPa.

used in CMC determinations for only double-chain cationic surfactants at 30 °C. The other plots are not shown (see Supporting Information for data). The intersection point of two straight lines represents the usual critical micelle concentrations of these surfactants. The CMC values found from the break points in Figure 3 are listed in Table 2, along with CMC values for all studied surfactants. It can be seen from Table 1 that the CMC values decrease with increasing alkyl-chain length in all cationic surfactants. The obtained values are in good agreement with the values reported in the literature for Gemini and conventional surfactants. Twin-tail cationic surfactants such as dodecylalkyldimethylammonium bromide (12-0-12) and dimethylene-bis(alkyldimethylammonium bromide) (12-2-12) were synthesized by Bakshi and Kaur.[30]

While they find a similar value for the 12-2-12 surfactant, they found a 1.8×10^{-4} mol kg^{-1} value for the 12-0-12 surfactant. With increase in the length of hydrophobic portion of the surfactant molecule, the hydrophobicity of the molecule increases, and, hence, the micellization becomes favorable.

The CMC value is the highest value in DTAB solution as compared to other surfactant solutions. The lowest CMC value in the studied surfactants has been observed for the double-chain cationic surfactants 16-0-16. If a molecule has a small and hydrophilic spacer, at the aqueous solution−air interface, the packing of the hydrophobic groups in Geminis is closer than in comparable meric ones. In a Gemini surfactant molecule two hydrophobic chain are more solvent structure-disruptive than an individual chain.[31] The CMC of 12-2-12 is about 15 times less than that of DTAB and that of 16-2-16 about 23 times less than that of CTAB. Also, 16-0-16 molecules do not have a spacer but have the double hydrocarbon chain, so that the tighter packing of the double-chain surfactant leads to a smaller CMC.

The degree of micelle ionization (α) is the number of counterions not bound to the micelle. Taking the ratio between the slopes above and below the linear portions of the break point in the conductivity graphics, the degrees of micelle ionization (α) were found and are also shown in Table 1. It can be seen from Table 2 that an increase in alkyl-chain length of the surfactant molecule results in an increase in the micelle ionization degree. The monomeric surfactants DTAB and CTAB have considerably higher α values than the other surfactants.

According to the α values, we can obtain the degree of counterion binding to micelle (β) ($\beta = 1 - \alpha$). These values show a trend to decrease with an increase in alkyl-chain length of surfactant molecule (see Table 2).The electrostatic force or Coulombic interaction between two opposite charges causes counterion binding.[32] In this study, we obtained higher β values for *m*-0-*m* surfactants than those of the *m*-2-*m* surfactants and corresponding monomeric surfactants. This state explains that, in (*m*-0-*m*) type surfactants, the ability of the Br^- counterion is stronger than that of the *m*-2-*m* surfactants, and in the *m*-2-*m* type surfactants, the ability of the Br^- counterion is stronger than that of the monomeric surfactants. Spacer and double-chain may be the reason for this result.

3.2. Krafft Temperature. The points of abrupt change in conductivity against temperature graphs were taken as Krafft temperature values, and only two of the graphs (12-2-12 and 12-0 12) are shown in Figures 1 and 2. Also, similar plots were obtained in pure water and in the presence of NaCl for all cationic surfactants. The K_T values evaluated from such plots in the absence and presence of electrolyte are summarized in Table 3. Moreover, the melting temperature values of cationic surfactants studied are given in this table.

3.3. Effect of the Length of the Surfactant Alkyl Chain. In Table 3, comparison of the results for the *m*-2-*m* series [for $m = 12$ and 16] Gemini surfactants shows that T_K and T_M increase with hydrophobic chain length, increasing alkyl chain length. The 10-2-10 Gemini surfactant has a Krafft point value below 0 °C,[12] and so, the effect of electrolyte on the Krafft point of this surfactant has not been investigated in the present work. 12-2-12 and 16-2-16 Gemini surfactants have Krafft point values of 15.5 and 44.1 °C, respectively. These values explain that the addition of the alkyl group increases the Krafft temperature. The same situation was observed for double-chain cationic surfactants. The 10-0-10, 12-0-12, and 16-0-16 double-chain cationic surfactants have Krafft temperature values of 19.8, 34.4, and 35.3 °C, respectively. This change on Krafft point can be due to either a change in monomer solubility or a change in the stability of the solid state. It is known that molecules which have the greatest number of alkyl groups will have the strongest hydrophobic interaction. The stability of the *m*-2-*m* surfactant monolayer increases as the hydrophobic chain length increases.[33] An increase in length of hydrophobic chain makes the aggregates in the bulk, thereby causing a reduction in surfactant solubility and, consequently, an increase in K_T value.[34] In two-headed dicationic surfactants, the headgroup has a high charge density; therefore, the result is not surprising. As seen in Figure 4, the Krafft temperatures follow in linear relationships based on the number of carbons in the hydrophobic chains for Gemini surfactants studied here. Also, there is a deviation from linearity for double-chain cationic surfactants.

3.4. Effect of the Spacer. The shorter spacer may draw the two heads closer and enhance the density of alkyl chain in Gemini surfactants. As a result, the hydrophobic interaction of the alkyl chains is greatly strengthened, and the result is a small CMC.[35] Furthermore, in the case of cationic surfactants, the spacer reduces the intermolecular repulsion between the head groups. This situation leads to micelle formation at low CMC values. The absence of the spacer group, peculiar to this new

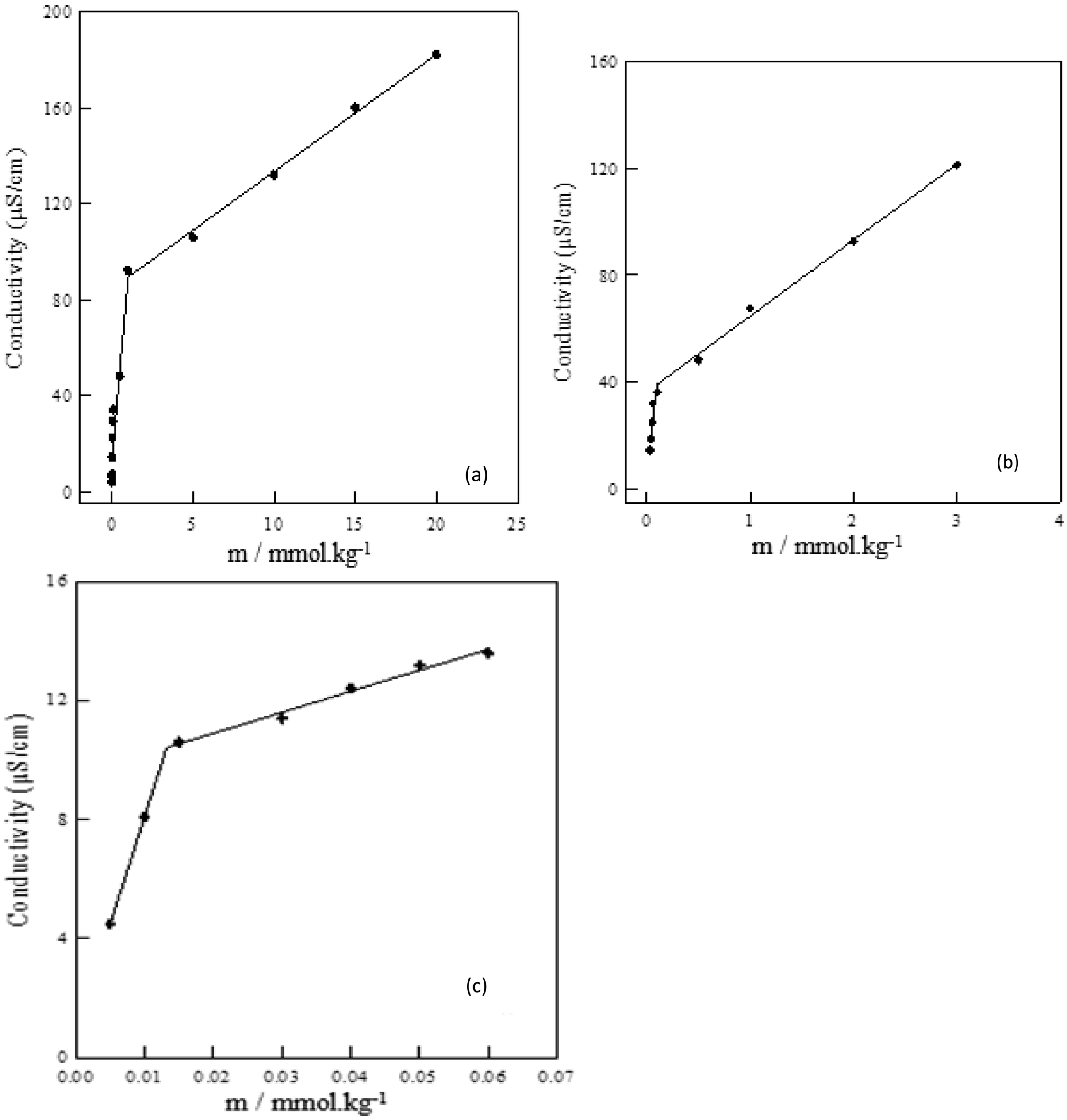


Figure 3. Plots of conductivity versus molality of double-chain cationic surfactants in pure water at 30 °C and 0.1 MPa: (a) 10-0-10, (b) 12-0-12, and (c) 16-0-16.

Table 3. Krafft Temperatures of Surfactants (1 wt %) as a Function of NaCl Molality and Melting Temperature[a] at 0.1 MPa

	surfactants (1 wt %)						
KP (°C)	DTAB	CTAB	12-2-12	16-2-16	10-0-10	12-2-12	16-0-16
pure	<0	25.8	15.5	43.2	19.8	34.4	35.3
0.01 (m/(mol kg^{-1}) NaCl	<0	24.5	14.7	42.3	17.7	32.5	32.8
0.02 (m/(mol kg^{-1}) NaCl	<0	23.1	14.1	41.4	16.4	32.1	30.0
0.03 (m/(mol kg^{-1}) NaCl	<0	21.5	10.4	41.0	15.5	31.4	29.5
0.04 (m/(mol kg^{-1}) NaCl	<0	20.0	9.9	40.6	15.3	31.3	29.0
0.05 (m/(mol kg^{-1}) NaCl	<0	18.7	9.4	40.3	15.2	31.2	28.8
MP (°C)	265.0	247.0	157.0	175.0	45.0	52.0	74.0

[a] The standard uncertainties for the Krafft Temperatures are $u(T_K)$ = 0.1 °C; the standard uncertainties for the melting temperatures are $u(T_M)$ = 0.5 °C, the standard uncertainties for surfactants in the solution are $u(s)$ = 0.001%, the standard uncertainties for molalities for NaCl are $u(m) = 1 \times 10^{-3}$ mol·kg^{-1}, and the standard uncertainties in u(p) are 0.01 MPa.

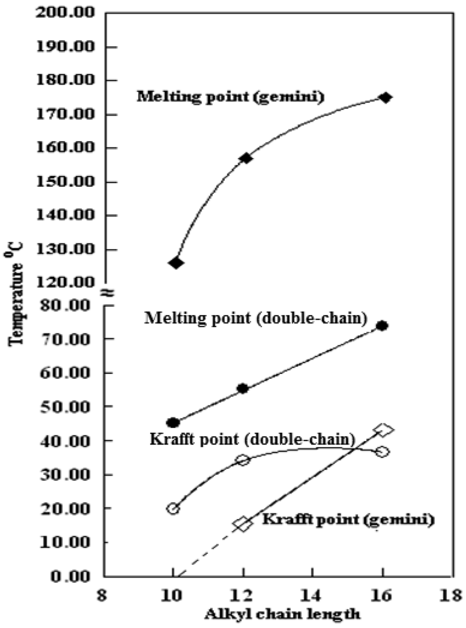


Figure 4. Variation of Krafft temperature, T_K, and melting temperature, T_M, for *m*-2-*m* Gemini surfactants (*m* = 12, 16) and *m*-0-*m* double-chain cationic surfactant (*m* = 10, 12, and 16). The T_K value of the 10-2-10 system is below 0 °C.

series of Gemini surfactants, may confer relatively low flexibility to the molecules, with potential implications on the interfacial properties, namely, on micellization. The results in Table 3 show that the same hydrophobic groups containing double-chain cationic surfactants have larger T_K values than those of Gemini surfactants. When the same hydrophobic groups containing Gemini and double-chain cationic surfactants are compared, the CMC values for 10-0-10 are about 600 times smaller than those of 10-2-10, while the values for 12-0-12 are about 19 times smaller than that of 12-2-12. On the contrary, this situation is different for 16-0-16. The T_K value for 16-0-16 is not larger than that of 16-2-16. The Krafft temperatures of a Gemini, of double-chain cationic surfactants, and of the corresponding monomeric surfactant can be directly compared in Figure 4. The T_K for 12-0-12, 12-2-12, and DTAB monomer of 12-2-12 are found as 34.4 °C, 15.5 °C, and below 0 °C, respectively. When compared to results for the 12-2-12 and DTAB, it shows that T_K values increased for the Gemini surfactant. The spacer group has decreased the T_K value. Those for 16-0-16, 16-2-16, and CTAB as a monomer of 16-2-16 are 35.3 °C, 43.2 °C, and 25.8 °C. Here, the spacer group has increased the T_K value.

3.5. Electrolyte Effect on the Krafft Temperature. The Krafft temperatures of the cationic surfactants (10-0-10, 12-0-12, 16-0-16, 10-2-10, 12-2-12, 16-2-16, DTAB, and CTAB) in pure water as well as in the presence of NaCl have been carried out at fixed surfactant concentration of 0.01 mol dm^{-3}. As seen in Table 3, K_T values decrease with increasing NaCl concentration for all cationic surfactants. Figure 5 shows the effect of NaCl addition on the Krafft temperature of 1 wt % aqueous Gemini surfactants 12-2-12 and 16-2-16 and conventional surfactants CTAB. The depression of T_K of cationic surfactants in the presence of an added NaCl is low. A linear relationship between Krafft temperature and NaCl concentration was observed in Figure 5. The T_K value is found to be 25.8 °C for CTAB in pure water and is in good agreement with the literature value.[23] It is sometimes difficult to determine how the addition of electrolytes changes the Krafft temperature, because the change depends on the effect of anions and cations. Usually, the addition of electrolytes reduces the CMC of surfactants, favoring their practical use. However, added electrolytes raise the T_K, which is obviously unfavorable for industrial applications. The presence of Br$^-$ raises, while that of Cl$^-$ lowers, the T_K of CTAB.[36] To explain the effect of Cl$^-$ and Br$^-$ on the T_K, two factors must be considered simultaneously: The salting-in behavior of the ions, along with the common ion effect on the solubility of CTAB.[37] It is known that ions with a low charge to radius ratio, such as Cl$^-$ and Br$^-$, are structure-breaking. Cl$^-$ possesses a higher hydration tendency than Br$^-$. This would mean that the solubility of surfactants increases in the presence of Cl$^-$ because of an increase in the hydration of the surfactant with a consequent decrease in the T_K. In this study, we have investigated the effect of NaCl molality on the Krafft temperature of various surfactant series. Figure 6 shows the effect of NaCl addition on the Krafft temperature of 1 wt % aqueous dicationic Gemini surfactants 10-0-10, 12-0-12, and 16-0-16 and conventional surfactants CTAB. It can be seen from Figure 5 that the relationship with Krafft temperature and NaCl molality was not exactly linear for double-chain cationic surfactants. It was observed that a gradual decrease was observed after the initial rapid decrease for these double-chain cationic surfactants.

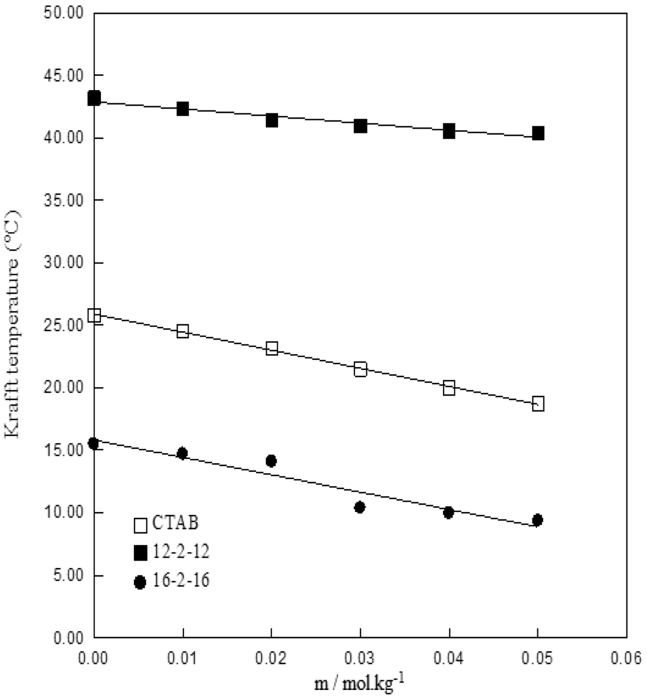


Figure 5. Effect of NaCl molalities on the Krafft temperature of conventional and Gemini surfactants (1% aqueous solutions): [CTAB, 12-2-12, and 16-2-16].

3.6. Melting Temperature of Surfactants. The melting point of an organic compound is strongly related to its structure. It has previously been noted that the Krafft temperature of a surfactant may be related to its melting temperature T_M.[27,38] The variation of T_M and T_K with alkyl chain length in Figure 4 shows some correlation, so that both T_M and T_K increase with the length of hydrocarbon chain. The melting temperatures of all the cationic surfactants studied are listed in Table 3. Melting temperatures of Gemini surfactants

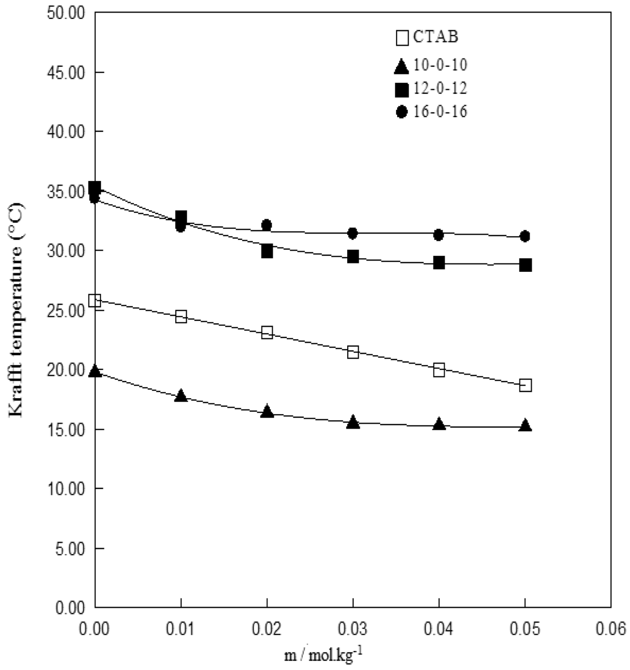


Figure 6. Effect of NaCl molalities on the Krafft temperature of conventional and double-chain cationic surfactants (1% aqueous solutions): [CTAB, 10-0-12, 12-0-12, and 16-2-16].

are higher than those of double-chain cationic surfactants, contrary to the variation of their Krafft temperature. Thus, the data indicate that there is a difference in the effects of the spacer group and of the alkyl chain carbon number on the properties of such cationic surfactants.

■ CONCLUSIONS

We have synthesized, purified, and characterized a series of novel Gemini surfactants without a spacer group, two tail—one head and two tail—two head surfactants. Conductivity measurements were used to examine the CMC values and the influence of NaCl molalities on Krafft temperatures of surfactants in aqueous solutions. The experimental results compared to each other, that is to say, T_K and T_M values increased with increase in the length of the hydrophobic alkyl group.

The results show that the Krafft temperature of the surfactants decreases with increase of the molality of NaCl in all cases. Also, surfactants with low Krafft temperature can be active in cold solutions, and this favors their practical use. These cationic surfactants possess extreme surface activity, and therefore they used many applications such as in nanotechnology in gene transfection and in the preparation of composite materials. Furthermore, Gemini surfactants have low CMCs; hence, they are used in new cosmetic and toiletry formulation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00367.

^{1}H NMR spectra and ^{13}C NMR spectra of 12-2-12 (PDF)

^{1}H NMR spectra and ^{13}C NMR spectra of 16-2-16 and ^{1}H NMR spectra and ^{13}C NMR spectra of 10-0-10 (PDF)

^{1}H NMR spectra and ^{13}C NMR spectra of 12-0-12 and ^{1}H NMR spectra and ^{13}C NMR spectra of 16-0-16 (PDF)

Tables showing the variation of conductivity with surfactant molalities and temperature dependence of the conductivity (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Akbaş, H.; Taner, T. Spectroscopic studies of interactions between C.I. Reactive Orange 16 with alkyltrimethylammonium bromide surfactants. *Spectrochim. Acta, Part A* **2009**, *73*, 150−153.

(2) Akbaş, H.; Kartal, C. I. Reactive Orange 16-dodecylpyridinium chloride interactions in electrolytic solutions. *Spectrochim. Acta, Part A* **2006**, *65*, 95−99.

(3) Menger, F. M.; Littau, C. A. Gemini surfactants: Synthesis and properties. *J. Am. Chem. Soc.* **1991**, *113*, 1451−1452.

(4) Zana, R. Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. *Adv. Colloid Interface Sci.* **2002**, *97*, 205−253.

(5) Zheng, Q.; Zhao, J. X. Solubilization of pyrene in aqueous micellar solutions of gemini surfactants C_{12}-*s*-C_{12}·2Br. *J. Colloid Interface Sci.* **2006**, *300*, 749−754.

(6) Rosen, M. J. Geminis: a new generation of surfactants. *CHEMTECH* **1993**, *23*, 30−33.

(7) Esumi, K. Ueno, M. *Structure performance relationship in surfactants*, 2nd ed.; CRC Press: New York, 1997.

(8) Grosmaire, L.; Chorro, M.; Chorro, C.; Partyka, S.; Zana, R. Alkanediyl-α, ω- bis(dimethylalkylammonium bromide) surfactants. Effect of the spacer carbon number and temperature on the enthalpy of micellization. *J. Colloid Interface Sci.* **2002**, *246*, 175−181.

(9) Akbaş, H.; Elemenli, A.; Boz, M. Aggregation and thermodynamic properties of some cationic Gemini surfactants. *J. Surfactants Deterg.* **2012**, *15*, 33−40.

(10) Kabir-ud-Din; Koya, P. A. Effects of solvent media and temperature on the self-aggregation of cationic dimeric surfactant 14−6-14, 2Br- studied by conductometric and fluorescence techniques. *Langmuir* **2010**, *26*, 7905−7914.

(11) Sohrabi, B.; Bazyari, A.; Hashemianzadeh, M. Effect of ethylene glycol on micellization and surface properties of Gemini surfactant solutions. *Colloids Surf., A* **2010**, *364*, 87−93.

(12) Akbaş, H.; Boz, M.; Batıgöç, Ç. Study on cloud points of Triton X-100-cationic Gemini surfactants mixtures: A spectroscopic approach. *Spectrochim. Acta, Part A* **2010**, *75*, 671−677.

(13) Sharma, K. S.; Hassan, P. A.; Rakshit, A. K. Self aggregation of binary surfactant mixtures of a cationic dimeric (Gemini) surfactant with nonionic surfactants in aqueous medium. *Colloids Surf., A* **2006**, *289*, 17−24.

(14) Ghosh, S. Surface chemical and micellar properties of binary and ternary surfactant mixtures (Cetyl pyridinium chloride, Tween-40 and Brij-56) in an aqueous medium. *J. Colloid Interface Sci.* **2001**, *244*, 128−138.

(15) Tikariha, D.; Kumar, B.; Ghosh, S.; Tiwari, A. K.; Saha, S. K.; Barbero, N.; Quagliotto, P.; Ghosh, K. K. Interaction between Cationic Gemini and monomeric surfactants: Micellar and surface properties. *J. Nanofluids* **2013**, *2*, 316−324.

(16) Akbaş, H.; Elemenli, A.; Batıgöç, Ç; Boz, M. Thermodynamic study of the interaction between C.I. Reactive Red 180 with Cationic Gemini surfactant in aqueous solution. *Asian J. Chem.* **2013**, *24*, 574−5752.

(17) Batıgöç, Ç.; Akbaş, H.; Boz, M. Micellization behaviour and thermodynamic parameters of 12−2-12 Gemini surfactant in (water + organic solvent) **mixtures**. *J. Chem. Thermodyn.* **2011**, *43*, 1349−1354.

(18) Menger, F. M.; Peresypkin, A. V. A combinatorially-derived structural phase diagram for zwitterionic Geminis. *J. Am. Chem. Soc.* **2001**, *123*, 5614−5615.

(19) Oda, R.; HuC, I.; Candau, S. J. Gemini surfactants as new, low molecular weight gelators of organic solvents and water. *Angew. Chem., Int. Ed.* **1998**, *37*, 2689−2691.

(20) Haas, S.; Hoffmann, H.; Thunig, C.; Hoinkis, H. Phase and aggregation behaviour of double-chain cationic surfactants from the class of **N**- alkyl-**N**-alkyl′-**N**, **N** -dimethyl ammonium bromide surfactants. *Colloid Polym. Sci.* **1999**, *277*, 856−867.

(21) Manousakis, M.; Avranas, A. J. Dynamic surface tension studies of mixtures of hydroxy propylmethyl cellulose with the double chain cationic surfactants didodecyldimethyl ammonium bromide and ditetradecyldimethylammonium bromide. *J. Colloid Interface Sci.* **2013**, *402*, 237−245.

(22) Bakshi, M. S.; Sachar, S.; Kaur, G.; Bhandari, P.; Biesinger, M. C.; Possmayer, F.; Petersen, N. O.; KAUR, G. Dependence of crystal growth of gold nanoparticles on the capping behavior of surfactant at ambient conditions. *Cryst. Growth Des.* **2008**, *8*, 1713−1719.

(23) Vautier-Giongo, C.; Bales, B. L. Estimate of the ionization degree of ionic micelles based on Krafft temperature measurements. *J. Phys. Chem. B* **2003**, *107*, 5398−5403.

(24) Zana, R.; Benraou, M.; Rueff, R. Alkanediyl-α,ω−bis-(dimethylalky1ammonium bromide) surfactants 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. *Langmuir* **1991**, *7*, 1072−1075.

(25) Menger, F. M.; Keiper, J. S.; Azov, V. V. Gemini surfactants with acetylenic spacers. *Langmuir* **2000**, *16*, 2062−2067.

(26) Chlebicki, J.; Wegrzynska, J.; Wilk, K. A. Surface-active, micellar, and anti electro-static properties of bis-ammonium salts. *J. Colloid Interface Sci.* **2008**, *323*, 372−378.

(27) Zana, R. Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants: II. Krafft temperature and melting temperature. *J. Colloid Interface Sci.* **2002**, *252*, 259−261.

(28) Moroi, Y. *Micelles, theoretical and applied aspects*; Plenum: New York, 1992.

(29) Tsuj, K. *Surface activity, principles, phenomenon, and applications*; Academic Press: New York, 1992.

(30) Bakshi, M. S.; Kaur, G. Mixed micelles of series monomeric and dimeric cationic, zwitterionic, and unequal twin-tail cationic surfactants with sugar surfactants: A fluorescence study. *J. Colloid Interface Sci.* **2005**, *289*, 551−559.

(31) Hait, S. K.; Moulik, S. P. Gemini surfactants: A distinct class of self-assempling molecules. *Curr. Sci.* **2002**, *82*, 1101−1111.

(32) Inoue, T.; Ebina, H.; Dong, B.; Zheng, L. Q. Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. *J. Colloid Interface Sci.* **2007**, *314*, 236−378.

(33) Wang, Y. J.; Marques, E. F.; Pereira, C. M. Monolayers of gemini surfactants and their catanionic mixtures with sodium dodecyl sulfate at the air-water interface: chain length and composition effects. *Thin Solid Films* **2008**, *516*, 7458−7466.

(34) Nong, L.; Xiao, C.; Zhong, Z. Physicochemical properties of novel phosphobetaine zwitterionic surfactants and mixed systems with an anionic surfactant. *J. Surfactants Deterg.* **2011**, *14*, 433−438.

(35) Danino, D.; Talmon, Y.; Zana, R. Alkanediyl-α,ω-bis-(dimethylalkylammonium bromide) surfactants (Dimeric Surfactants). 5. Aggregation and microstructure in aqueous solutions. *Langmuir* **1995**, *11*, 1448−1456.

(36) Roy, J. C.; Islam, Md. N.; Aktaruzzaman, G. The effect of NaCl on the Krafft temperature and related behavior of cetyltrimethylammonium bromide in aqueous solution. *J. Surfactants Deterg.* **2014**, *17*, 231−242.

(37) Pegram, L. M.; Record, M. T. Thermodynamic origin of Hofmeister ion effects. *J. Phys. Chem. B* **2008**, *112*, 9428−9436.

(38) Shinoda, K.; Hato, M.; Hayashi, T. Physicochemical properties of aqueous solutions of fluorinated surfactants. *J. Phys. Chem.* **1972**, *76*, 909−914.