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Spontaneous Formation of Nanocubic Particles and Spherical Vesicles in Catanionic Mixtures of Ester-Containing Gemini Surfactants and Sodium Dodecyl Sulfate in the Presence of Electrolyte

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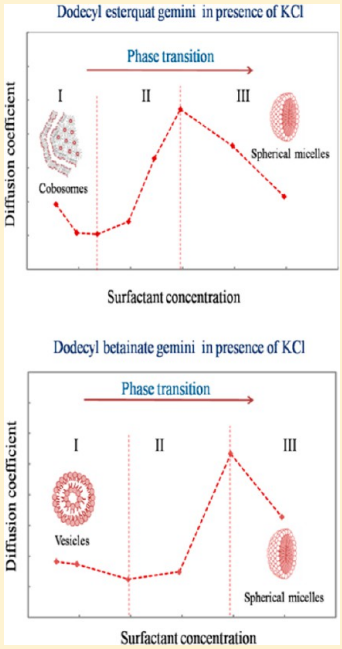
Supporting Information

ABSTRACT: Self-assembly of pure ester-containing cationic gemini surfactants, dodecyl esterquat, and dodecyl betainate geminis, and cation-rich catanionic mixtures of them with sodium dodecyl sulfate (SDS) were investigated using surface tension, electrical conductivity, dynamic light scattering (DLS), transmission electron microscopy (TEM) and cyclic voltammetry (CV) measurements in the absence and presence of KCl. Different physicochemical properties such as the critical micelle concentration (CMC), degree of counterion dissociation (α_{diss}), interfacial properties, morphology of aggregates, and interparticle interaction parameters were determined. Both geminis formed micelles in the absence of KCl, and mixing with SDS did not change the morphology; just a growth in micelle size was observed. However, the aggregation behavior of these geminis with respect to the position of the ester bond in the alkyl chain appeared completely different in the presence of KCl. Esterquat gemini formed cubic nanoparticles (or cobosomes) in the presence of [KCl] = 0.05 M and transformed into spherical micelles upon increasing the surfactant concentration. By contrast, betainate gemini formed vesicles in the presence of [KCl] = 0.05 M and subsequently converted to micelles as the surfactant concentration increased. The morphology of esterquat gemini (in the presence of 0.05 M KCl) after mixing with SDS changed from cubic nanoparticles (or cobosomes) to cylindrical nanoparticles coexistent with cobosomes. Betainate gemini remained vesicular upon mixing with SDS, and no dramatic structural change of aggregates took place. The morphology changes of aggregates upon mixing with SDS were explained from calculating the interactions between two gemini surfactants and SDS on the basis of regular solution theory.



1. INTRODUCTION

Cleavable surfactants are amphiphiles in which a weak linkage has been deliberately inserted, normally, but not always, between the hydrophobic tail and the polar headgroup.[1] The new environmental legislation for surfactants is the main driving force for development of cleavable surfcatants as there is often a connection between the hydrolysis rate and the rate of biodegradation.[2,3]

The dominating use of esterquats is as fabric softeners, and the transition from the traditional di(hydrogenated tallow)-dimethylammonium chloride to esterquats was done in Europe as a response to pressure from environmental authorities in the European Union in the early 1990s.[4]

Both chemical and enzymatic hydrolysis of betainesters yield the amino acid betaine and the starting alcohol, two products that can be considered environmentally compatible and probably even edible.[5] Thus, betainesters are interesting candidates for applications such as cosmetics, food, and feed.[6]

Gemini surfactants are characterized by two hydrophilic and hydrophobic groups that are linked by the spacer. The main reason for such an interest toward these novel surfactants is their higher surface activity and much lower critical micelle concentrations (CMC) than those of conventional monomeric surfactants. Cationic geminis are used as promising surfactants in detergency, as efficient transfection vehicles in regulation of gene expression and signal transduction,[7] the best ion exchangers on silica surfaces compared to nonionic and anionics[8] and have shown efficiency in skin care, antibacterial properties, and vesicle formation.[9] Gemini surfactants can replace their monomeric counterparts in a wide range of applications because of their higher efficiency and performance.[10,11] Before that can happen, they should meet two important criteria including the production cost and their

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Table 1. Interfacial, Thermodynamic, and Structural Parameters of Ester-Containing Gemini Surfactants[a]

parameter	symbol	equation
surface excess concentration[27]	Γ_{max}	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2} = \frac{-1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)_{T,P}$ (1)
minimum area per molecule[27]	A_{min}	$A_{min}/\text{nm}^2\cdot\text{molecule}^{-1} = \frac{10^{18}}{N_A\Gamma_{max}}$ (2)
surface activity[27]	pC_{20}	$pC_{20} = -\log C_{20}$ (3)
surface pressure[27]	π_{CMC}	$\pi_{CMC} = \gamma_o - \gamma_{CMC}$ (4)
Gibbs free energy of micellization[28,29]	ΔG°_{mic}	$\Delta G^o_{mic}/(\text{kJ}\cdot\text{mol}^{-1}) = RT(1.5 - \alpha_{diss})\ln X_{CMC}$ (5)
Gibbs free energy of adsorption[30]	ΔG°_{ads}	$\Delta G^o_{ads}/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta G^o_{mic} - \left(\frac{\Pi_{CMC}}{\Gamma_{max}}\right)$ (6)
mole fraction of SDS in the mixed micelle[31]	X_1	$\frac{(X_1)^2\ln(\alpha_1 C_{12}^M/X_1C_1^M)}{(1-X_1)^2\ln[(1-\alpha_1)]C_{12}^M/(1-X_1)C_2^M} = 1$ (7)
interaction parameter for mixed micelle[31]	β^M	$\beta^M = \frac{\ln[\alpha_1 C_{12}^M/X_1C_1^M]}{(1-X_1)^2}$ (8)
activity coefficient of SDS[31]	f_1	$f_1 = \exp[\beta(1-X_1)^2]$ (9)
activity coefficient of gemini surfactants[31]	f_2	$f_2 = \exp[\beta(X_1)^2]$ (10)
mole fraction of SDS in the total mixed monolayer[32]	Z_1	$\frac{Z_1^2\ln(\alpha_1 C_{12}Z_1C_1^0)}{(1-Z_1)^2\ln[(1-\alpha_1)]C_{12}/(1-Z_1)C_2^0} = 1$ (11)
interaction parameter for mixed monolayer at the aqueous solution/air interface[32]	β^σ	$\beta^\sigma = \frac{\ln(\alpha_1 C_{12}/Z_1C_1^0)}{(1-Z_1)^2}$ (12)
ideal mixing minimum area per molecule[33]	A_{ideal}	$A_{ideal} = Z_1A_1 + (1-Z_1)A_2$ (13)
excess free energy of micellization according to regular solution theory[34]	G^{ex}_{mic}	$G^{ex}_{mic} = RT[X_1\ln f_1 + (1-X_1)\ln f_2]$ (14)
experimental excess free energy of micellization[35]	(G^{ex}_{mic}) exp	$(G^{ex}_{mic})_{exp} = \Delta G^0_{mic,mix} - [X_1\Delta G^0_{mic,1} + (1-X_1)\Delta G^0_{mic,2}]$ (15)
diffusion coefficient of the ferrocene probe[36]	D_{agg}	$i_{p_a} = 0.4463FACn\left(\frac{nF\nu D_{agg}}{RT}\right)^{1/2}$ (16)
interparticle interaction parameter[37]	k_d	$D_{agg} = D^0_{agg}[1 - k_d(C_s - \text{CMC})]$ (17)
mean hydrodynamic radius in CV measurements[38]	R_h	$R_h = \frac{kT}{6\pi\eta D_{agg}}$ (18)

[a]More information about symbols in equations is in the Supporting Information.

environmental impact. The concept of producing a cleavable gemini surfactant is one way to meet the later criterion (i.e., producing a biodegradable surfactant). Thus, the importance of the current study should be seen from this standpoint and as a way for developing novel cleavable gemini surfactants with higher performance and efficiency and studying their physiochemical properties in various applications.

It is well-known that aqueous mixtures of anionic and cationic surfactants have unique phase behavior and physiochemical properties that arise from the strong electrostatic interactions between oppositely charged head groups.[12] The partial neutralization of the micellar surface charge results in strong release of counterions, causing entropy increase that drives the aggregation.[13] For example, a stable vesicle, a long rod-like micelle, or a cylindrical micelle can be formed at appropriate ratios of anionic-to-cationic surfactants. Vesicles are not only interesting because they mimic biological membranes, but they have also recently been used in applications such as drug delivery, nanotechnology,[14] and two-dimensional crystallization of proteins.[15]

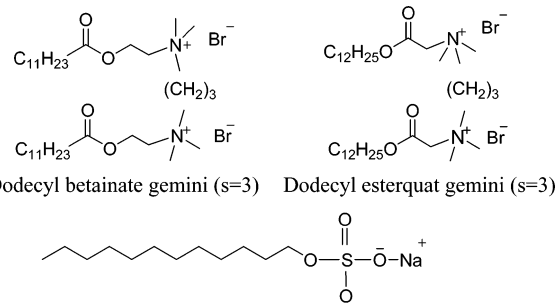
An important characteristic of those mixtures is their strong synergistic interactions, manifested by low CMC and enhanced surface activity. Given the growing demands of industrial technology, the search for high performance surface active compounds is increasing. One such attempt is gemini-conventional surfactant mixtures, which would be superior on the application front compared to pure systems. The presence of two charged sites in a gemini proposes stronger interaction with the neutral and oppositely charged ionic surfactants compared to that of the conventional surfactant mixtures.[16] This is one approach for reducing the price of the final product by formulating and mixing different surface active materials. However, most published studies concern mixtures of traditional surfactants; only a limited number of attempts have been made regarding mixed micellization of the gemini and single-chain surfactants.[17−20] Recently, some ester-containing gemini surfactants have been synthesized and their physicochemical properties and aggregation behavior have been studied.[21−24] Mixed micellization of similar gemini surfactants with anionic, cationic, and nonionic conventional surfactants was also studied by Fatma et al.[25,26] However, the influences of direction of ester bond on self-assemblies of ester-containing cationic gemini surfactants and catanionic mixtures of them with SDS have not yet been fully understood. Hence, the aim of the present work

is studying the effect of ester bond position on physicochemical properties, size, and morphology of ester-containing cationic gemini surfactants, esterquat and betainate geminis, and their mixtures with SDS in the absence and presence of KCl. The interfacial, thermodynamic and structural properties (Table 1), and aggregation behavior have been comprehensively studied using conductometry, tensiometry, dynamic light scattering (DLS), and transmission electron microscopy (TEM) techniques. Cyclic voltammetry has also been used efficiently to investigate the phase transition observed at the studied concentration range.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. The ester-containing gemini surfactants (Scheme 1) were synthesized according to the previous reports.[2,24] Sodium dodecyl sulfate (SDS), potassium chloride (KCl), and ferrocene were obtained from Merck and used without further purification. Doubly distilled deionized water was used for sample preparation and dilution. A fresh surfactant solution was prepared for each series of measurements. It should be noted that when esterquat and betainate geminis are present in an unbuffered aqueous solution, the initial hydrolysis leads to a lowering of the pH to values at which the compound is stable.[5] In our experiments, the pH of esterquat gemini and betainate gemini solutions was in the range of (5.6 ± 0.2) and (4.9 ± 0.2), respectively.

Scheme 1. The Structure of Studied Surfactants



The binary gemini-SDS solutions at various mole fractions of SDS were prepared, and their phase behavior was investigated visually. Mixed cationic gemini-anionic surfactant systems precipitate easily in aqueous solutions because of strong interactions between headgroups of the opposite charge. Only in the cationic-rich regime the solutions were homogeneous, and no precipitate was observed (see Supporting Information). Then, further experiments are carried out in the rich cationic region.

2.2. Methods. *(a). Surface Tension Measurements.* The equilibrium surface tension as a function of surfactant concentration was measured by a Krüss K12 tensiometer under atmospheric pressure by the ring method.[39] The platinum ring was thoroughly cleaned with acetone and then flame-dried before each measurement. The uncertainty of the measurements was ±0.1 $mN \cdot m^{-1}$. At least three measurements were carried out for each data point, and the standard deviation did not exceed 0.08 $mN \cdot m^{-1}$. The temperature was maintained constant by circulating thermostatted water through a jacketed vessel containing the solution. The temperature was controlled within ±0.1 K.

(b). Electrical Conductivity Measurements. The specific conductivity as a function of surfactant concentration was measured by a Jenway 4510 conductometer using a water bath with stirring to control the temperature. For each series of measurements, the conductivity of an exact volume of 50 mL doubly distilled deionized water was measured. The solution was then titrated with the surfactant solution, and the conductivity was measured after each titration under controlled constant temperature. The uncertainty of the measurements was in the range of ±0.01 $\mu S \cdot cm^{-1}$.

(c). Dynamic Light Scattering Measurement. Size and zeta potential of solutions were measured with a Malvern zetasizer (model nano-ZS). Fresh surfactant solutions were used for each measurement, and the refractive index and viscosity of the solutions were determined. The refractive index was determined using a Krüss digital refractometer model DR 201-95. Viscosity measurements were carried out using an Ubbelohde viscometer (model FUNGILAB S. A., size 0C) suspended vertically in a thermostat at 298 ± 0.1 K.

(d). Cyclic Voltammetry Measurements. Cyclic voltammetry measurements were performed using a SAMA 500 electroanalyzer system at 298 K, with electro-active probe of ferrocene. A three-electrode system composed of a platinum disk electrode (0.0314 cm^2) as the working electrode, a platinum foil (2 cm^2) as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode was used for CV measurements. All solutions were prepared to a final volume of 25 mL, containing 0.05 M KCl, 0.001 M ferrocene, and different concentrations of surfactants. Due to the insolubility of ferrocene in water, ferrocene was first dissolved in ethanol before the small volume of the resulting ethanol solution was added to the aqueous surfactant solution. The small volume of the ethanol solution compared to the final solution volume meant that the effects of ethanol were negligible.[33] The working electrode was polished and then rinsed by distilled water before recording each voltammogram. All voltammograms were recorded with a scan rate of 100 $mV \cdot s^{-1}$, and the third cycles were saved.

(e). Transmission Electron Microscopy (TEM). Transmission electron micrographs were recorded on a Zeiss electron microscope (model EM10C) operated at 80 kV. Samples were placed on carbon-coated grids and kept waiting for the solvent to evaporate, and then micrographs were obtained.

3. RESULTS AND DISCUSSION

3.1. Determination of CMC and Surfactant−Surfactant Interactions in the Aggregated Phase. *(a). In the Absence of KCl.* The CMC values of the pure esterquat gemini and betainate gemini and their mixtures with SDS (in the cationic-rich regime) in aqueous solutions at 298 K were determined from surface tension measurements and conductivity plots (Figures 1 and 2) as shown in Table 2. It should be noted that there was precipitate in betainate gemini/SDS solution at α_{SDS} = 0.2 and no measurement was done. According to Table 2, a sharp decrease was seen in CMC values for esterquat gemini upon mixing with SDS. Contrarily, the CMC of betainate gemini remained constant and no dramatic change was observed due to addition of SDS. The CMC values (Table 2) obtained from conductometry were in agreement with tensiometry in pure esterquat and betainate geminis, SDS and betainate gemini/SDS (α_{SDS} = 0.1) systems and no second CMCs were observed. In esterquat gemini/SDS systems (both α_{SDS} = 0.1 and α_{SDS} = 0.2), the CMC values obtained from

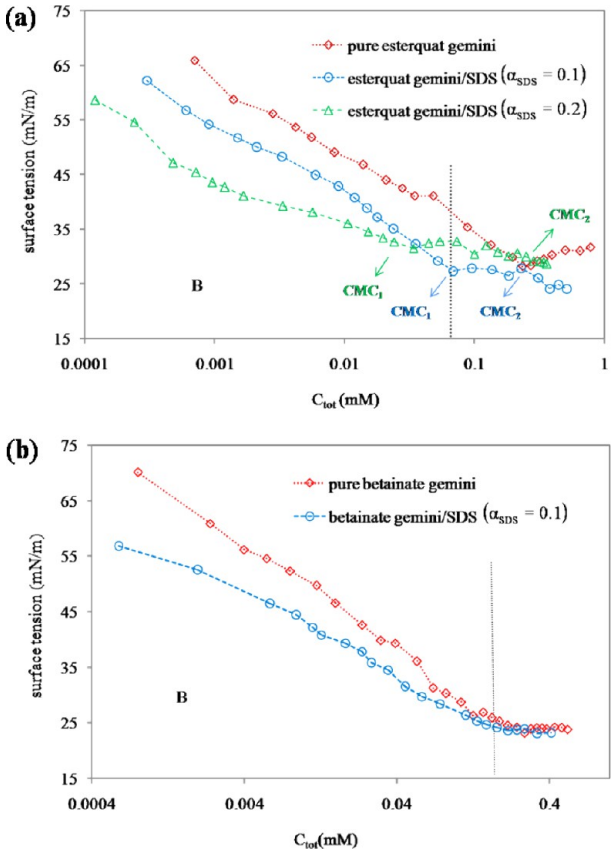


Figure 1. Surface tension versus total surfactant concentration at 298 K.

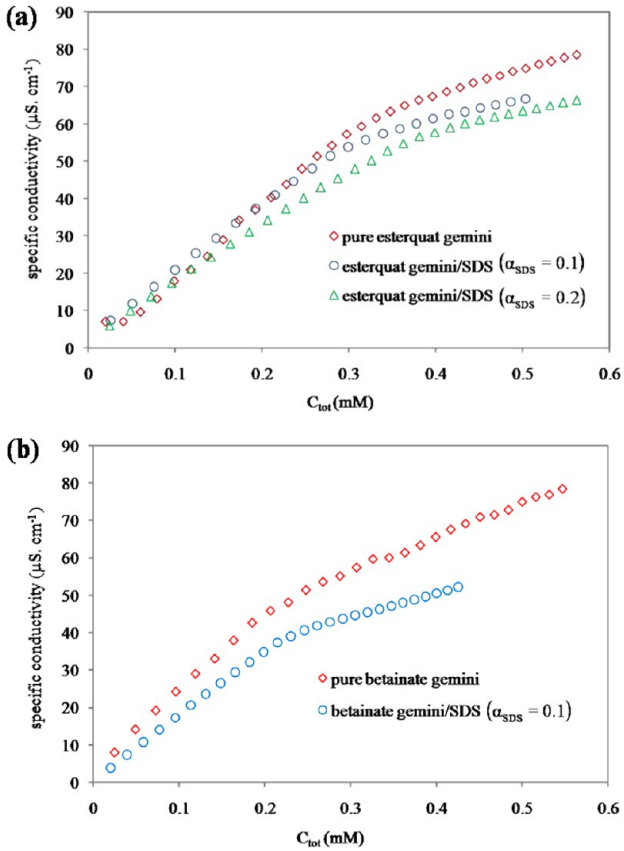


Figure 2. Specific conductivity versus total surfactant concentration at 298 K.

conductometry were much higher than those of tensiometry. However, the γ−log C plot showed the second break near the conductance plot break, which may be due to the formation of a second state of aggregation.

The tensiometry detects smaller aggregates formed at lower concentrations while the conductometry is capable of detecting larger aggregates and not sensitive enough to detect the break at very low concentrations. Overall, it is inferred that tensiometry gives an accurate estimate of CMC. The first CMC corresponds to the formation of normal spherical micellar aggregates, while the second CMC is due to structural transformation. This behavior has also been reported in mixed CTAB/SDS and other mixed systems.[33,40] As it is expected, the CMC value of esterquat gemini/SDS system at α_{SDS} = 0.2 was lower than at α_{SDS} = 0.1.

When micelles are formed in solution, counterions bind with micellar surface. The degree of counterion dissosiation (α_{diss}) is an index of counterion binding to the micelle surface. More counterions are binded to the micelle surface as the value of α_{diss} is decreased. The α_{diss} values were extracted from conductomtry plots using Frahm's method[41] as listed in Table 2. It was observed that α_{diss}, did not change upon mixing with SDS for both geminis, in spite of entering SDS molecules into the geminis aggregates. The mentioned phenomenon is attributed to micellar growth, as indicated later by TEM (Figure 3).

The much lower CMC value for esterquat gemini/SDS compared to the betainate gemini/SDS system can be explained by micellar interaction parameter, β^M, (Table 1, eq 8) as listed in Table 3. The values of β^M for all mixed systems were negative, which indicates that after mixing, the interaction between geminis and SDS is more attractive or less repulsive compared to before mixing. As can be seen in Table 3, β^M was more negative for esterquat gemini/SDS (at both α_{SDS} = 0.1 and 0.2) than betainate gemini/SDS, showing more synergism for esterquat gemini/SDS system. The parameter β^M reflects two main Gibbs free energy contributions of mixed micellization. These are a free energy contribution associated with the interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, $\beta^{M,core}$, and an electrostatic contribution $\beta^{M,elec}$, related to electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2.[42] Esterquat and betainate geminis have the same hydrophobic tail, and the interactions between their hydrophobic groups with SDS ($\beta^{M,core}$) is similar, but since the position of ester bond differes, the electrostatic interactions between their charged hydrophilic groups with SDS ($\beta^{M,elec}$) is different. Therefore, $\beta^{M,elec}$ has dominant contribution to the difference of β^M for these mixed systems.

In betainate gemini, the vicinity of the partially negative carbonyl group and the positive quaternary ammonium causes the positive charge to depart from the quaternary ammonium, so the electrostatic interactions between its charged hydrophilic groups with SDS decreases. This effect for esterquat gemini is less noticeable, and the electrostatic interactions between its charged hydrophilic groups and SDS is higher and more synergism could be observed for esterquat gemini/SDS system. In fact, the vicinity and direction of the carbonyl group to the quaternary ammonium in betainate gemini causes acting as a zwitterionic surfactant. Comparing the β^M values of zwitter-

Table 2. CMC, α_{diss}, and Thermodynamic Parameters of Micellization of Gemini Surfactants and Their Mixtures at 298 K

	system	CMC[a] (mM)	CMC[c] (mM)	α_{diss}	ΔG°_{mic}[d] (kJ·mol^{-1})	G_{mic}^{ex} (kJ·mol^{-1})	$(G_{mic}^{ex})_{exp}$ (kJ·mol^{-1})
in absence of 0.05 M KCl	esterquat gemini/SDS (α_{SDS} = 0.1)	0.069(0.24)[b]	0.3	0.34	−39.08	−5.62	−6.48
	esterquat gemini/SDS (α_{SDS} = 0.2)	0.024(0.25)[b]	0.32	0.37	−40.66	−8.78	−8.83
	betainate gemini/SDS (α_{SDS} = 0.1)	0.214	0.21	0.37	−34.96	−1.46	−2.67
	esterquat gemini	0.23	0.31	0.36	−35.26	-	-
	betainate gemini	0.24	0.23	0.41	−33.47	-	-
	SDS	7.74	8.50	0.33	−25.73	-	-
in presence of 0.05 M KCl	esterquat gemini/SDS (α_{SDS} = 0.1)	0.002	-	-	-	-	-
	betainate gemini/SDS (α_{SDS} = 0.1)	0.001	-	-	-	-	-
	esterquat gemini	0.003	-	-	-	-	-
	betainate gemini	0.001	-	-	-	-	-

[a]The values obtained from surface tension measurements. [b]The values in parentheses correspond to the second break in the γ−log C plot. [c]The values obtained from conductometry measurements. [d]ΔG°_{mic} were calculated by using the CMC values obtained from surface tension measurements and α_{diss} values obtained from conductometry measurements.

Table 3. Interaction Parameters of Mixed Systems at 298 K

	mixed micelle				mixed monolayer			
system	X_1	f_1	f_2	β^M	Z_1	f_1	f_2	β^σ
esterquat gemini/SDS (α_{SDS} = 0.1)	0.28	0.003	0.41	−11.16	0.26	0.0008	0.41	−13.07
esterquat gemini/SDS (α_{SDS} = 0.2)	0.36	0.0017	0.142	−15.35	0.37	0.0001	0.05	−22.27
betainate gemini/SDS (α_{SDS} = 0.1)	0.13	0.02	0.91	−5.21	0.22	0.0015	0.58	−10.77

Table 4. Interfacial Properties of Gemini Surfactants and Their Mixtures in the Absence of 0.05 M KCl at 298 K

system	$\Gamma_{max} \times 10^6$ (mol·m^{-2})	A_{min} (nm^2·molecule^{-1})	A_{ideal} (nm^2·molecule^{-1})	π_{CMC}	pC_{20}	ΔG°_{ads} (kJ·mol^{-1})
esterquat gemini/SDS (α_{SDS} = 0.1)	1.16	1.43	0.82	42.5	3.02	−75.72
esterquat gemini/SDS (α_{SDS} = 0.2)	0.69	2.41	0.78	36.46	3.32	−93.51
betainate gemini/SDS (α_{SDS} = 0.1)	0.90	1.85	1.20	43.49	2.24	−83.28
esterquat gemini	1.81	0.92	-	41.24	1.4	−57.57
betainate gemini	1.20	1.38	-	47.25	2.00	−72.84
SDS	3.02	0.55	-	40.83	0.19	−39.21

ionic/anionic mixed systems with β^M of the betainate gemini/SDS system reveals that as well. For example, for the $C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-/C_{12}H_{25}SO_3Na$ (sodium dodecyl solphonate) mixed system at pH = 5, the average β^M is −5.4.[43] The β^M of esterquat gemini/SDS system is in the β^M value range of a similar cationic gemini surfactant/anionic surfactant mixed system.[19,25] Fatma et. al has obtained the value of β^M = −13.04 for the $C_{12}H_{25}(CH_3)_2N^+$-$(CH_2COOCH_2)_2N^+(CH_3)_2C_{12}H_{25}$/SDS system at α_{gemini} = 0.2.[25]

The results showed that the mixed micelles of esterquat gemini/SDS contain a high fraction of SDS, whereas mixed micelles of betainate gemini/SDS have a low fraction of SDS (X_1 values are calculated from eq 7 and listed in Table 3).

As is expected, due to synergism, the ΔG°_{mic} values (Table 1, eq 5) for mixed systems were more negative than pure one's. The ΔG°_{mic} value for the esterquat gemini/SDS mixture was more negative than that of the betainate gemini/SDS system, indicating that the micelles of the esterquat gemini/SDS system form more spontaneously. The G_{mic}^{ex} values calculated from eq 14 and 15 are also listed in Table 2. As can be seen, there is a good agreement between the $(G_{mic}^{ex})_{exp}$ values calculated from eq 15 and that of regular solution theory (eq 14), showing that applying the regular solution theory to describe the interaction between gemini surfactant and SDS is an appropriate choice. The G_{mic}^{ex} and β^M values had the same trend. For the esterquat gemini/SDS (α_{SDS} = 0.2) system that showed the most synergism, the G_{mic}^{ex} had the most negative value.

(b). In the Presence of KCl. The CMC values for pure gemini surfactants and mixed systems in the presence of KCl were measured using tensiometry as shown in Table 2. The CMC value for SDS in the presence of [KCl] = 0.05 M could not be measured, because the precipitate formed in solution.[44] Consequently, the interaction parameters for mixed systems in the presence of KCl could not be calculated. The presence of KCl also causes the esterquat gemini/SDS solution at (α_{SDS} = 0.2) precipitate, and no further experiments were done in this case. Comparing the CMC values of pure gemini surfactants and mixed systems in the presence of KCl revealed that the presence of electrolyte has covered the synergistic effect of SDS on gemini surfactants, so that the CMC values of gemini surfactants did not change a lot upon mixing with SDS.

3.2. Interfacial Properties and Surfactant−Surfactant Interactions in a Monolayer at the Liquid−Air Interface.

The interfacial properties of gemini surfactants and their mixtures (Table 1, eqs 1−4,6) are shown in Table 4. Table 4 also shows the ideal mixing minimum area per molecule, A_{ideal}, calculated from eq 13.

The experimental A_{min} values extracted from the Gibbs equation in region B (Figure 1) bears an incorrect assumption, namely, that the interface is already saturated when the surface tension first begins its sudden reduction. Recently, Menger et al. have argued that the interface, in fact, is not saturated in region B.[45] The nonlinear curve fitting to linear region B somewhat improves the calculated molecular areas. The slope of the tangent at a given concentration of the γ versus log C

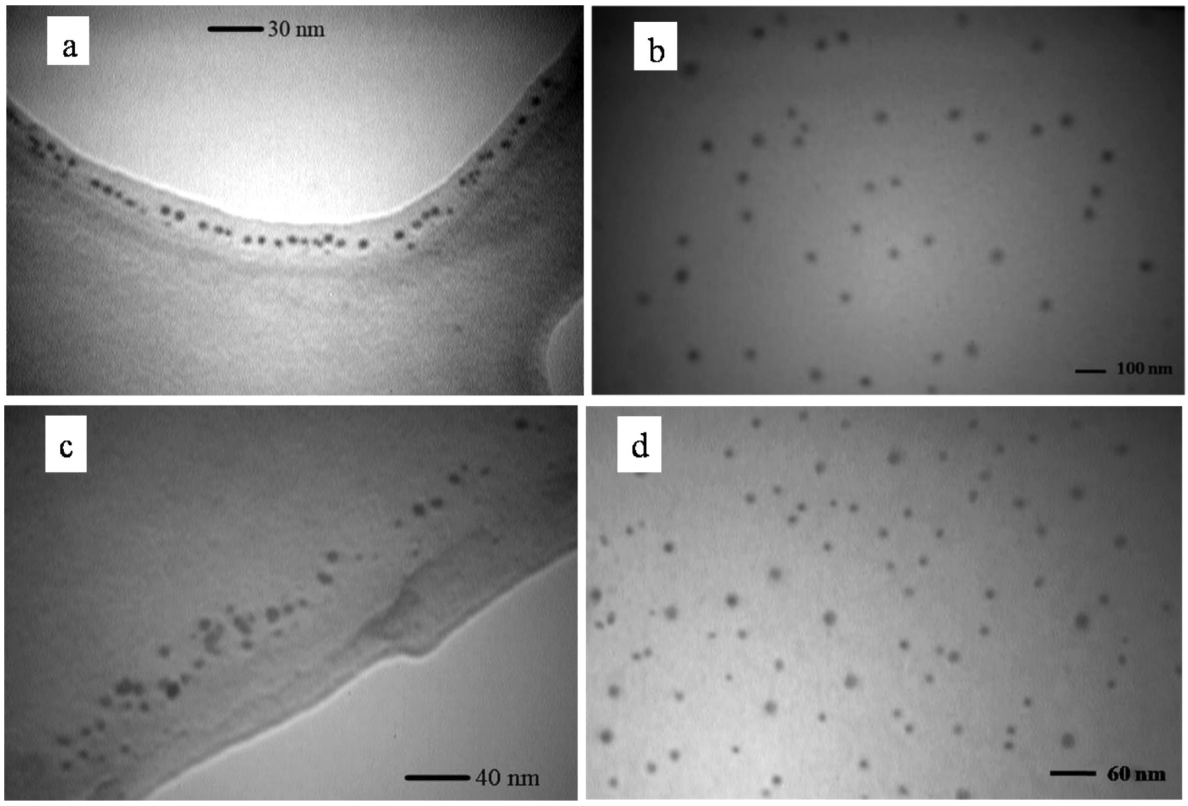


Figure 3. TEM images in the absence of 0.05 M KCl: (a) pure esterquat gemini (5 mM) and (b) esterquat gemini/SDS (α_{SDS} = 0.2) at C_{tot} = 5 mM, (c) pure betainate gemini (15 mM) and (d) betainate gemini/SDS (α_{SDS} = 0.1) at C_{tot} = 5 mM.

plot was used to calculate Γ_{max} by curve fitting to a quadratic equation.[46]

Table 4 shows that the Γ_{max} values of geminis decreased upon mixing with SDS. Regarding the strong attractive electrostatic interaction between cationic geminis and SDS, the formation and adsorption of bulkier gemini-SDS ion pairs is very probable. It is expected that these ion-pairs are more hydrophobic compared to both surfactants. Thus, the solution surface is simultaneously occupied with individual surfactants as well as with their ion pairs which is often observed for oppositely charged anionic/cationic systems.[45] Anyway, discussing these ion pairs and their orientation at surface needs further investigations. As expected, A_{min} demonstrated an inverse trend with respect to Γ_{max}.

The experimental A_{min} values were greater than A_{ideal}, in spite of the strong synergism between them ,which may be due to van der Waals self-attraction between the hydrophobic parts of each gemini before mixing, which is reduced upon mixing with SDS. The other reason can be the formation of hydrophobic ion-pairs that occupy higher surface area than those of pure surfactants.

The surface activity of pure gemini surfactants and mixed systems was determined using tensiometry plots. The surface activities (pC_{20}) of mixed systems were higher than each individual surfactant (Table 4), indicating higher tendency of formed ion-pairs toward interface. The pC_{20} for the esterquat gemini/SDS was also higher than that of betainate gemini/SDS system.

The ΔG°_{ads} values were found to be more negative than the corresponding ΔG°_{mic} (see Table 2 and 4). Both ΔG°_{mic} and ΔG°_{ads} were negative, and their magnitudes showed that micelle formation is less spontaneous compared to adsorption.

Table 3 shows the calculated β^{σ} (Table 1, eq 12) as an index of interaction parameter at the air/solution interface and for calculating it, the C_1^0, C_2^0 and C_{12}^0 were determined corresponding to a surface tension of 45.00 mN m^{-1} (see Figure 1). The values of β^{σ} for all mixed systems were also negative, indicating strong synergism between the cationic and anionic surfactants in monolayer. The β^{σ} values were more negative than β^{M} showing the greater electrostatic attraction energy between the cationic and anionic surfactants generated at the planar interface than in the convex micellar surface. This was in agreement with the more negative ΔG°_{ads} values in comparison to ΔG°_{mic} values. Similar to β^{M}, β^{σ} was also more negative for esterquat gemini/SDS (at both α_{SDS} = 0.1 and 0.2) than betainate gemini/SDS, showing smaller synergism for betainate gemini/SDS system. As mentioned above, the zwitterionic nature of betainate gemini results in a less attractive electrostatic interaction between its charged hydrophilic groups and SDS and, consequently, less synergism could be observed for the betainate gemini/SDS system.

3.3. Size, Morphology, and Interactions of Catanionic Self-Assemblies. *(a). In the Absence of KCl.* Dynamic light scattering (DLS) measurements provide insights into the overall micellar structure. Usually, a small size distribution with a hydrodynamic diameter of several nanometers for a surfactant corresponds to spherical micelles. Zeta potential is a measure of the electrical potential of a charged particle. Depending on the interaction of charged particle with the surrounding molecule or environment, its point charge is exposed to the solution, and hence the zeta potential is changed. Thus, the zeta potential also gives some information about molecular interaction of a species in solution and at interface.[47] Table 5 shows the mean diameter and zeta potential

Table 5. Mean Diameter and Zeta Potential of Gemini Surfactants and Mixed Systems at $[C_{tot}]$ = 15 mM in the Absence of KCl Obtained by DLS

system	mean diameter (nm)	zeta potential (mV)
esterquat gemini/SDS (α_{SDS} = 0.1)	2.4	57.1
	23.0	
	(12.7)[a]	
esterquat gemini/SDS (α_{SDS} = 0.2)	8.6	54.3
	60.2	
	(45.9)[a]	
betainate gemini/SDS (α_{SDS} = 0.1)	2.1	31.5
	13.1	
	(2.6),(16.7)[a]	
esterquat gemini	(1.9)[a]	85.6
	2.5	
betainate gemini	2.2	33.4
	10.6	
	(2.1),(9.8)[a]	

[a]Measured at $[C_{tot}]$ = 5 mM.

of gemini surfactants and mixed systems obtained by DLS (the corresponding diagrams are shown in Supporting Information). As can be seen from Table 5, changing the surfactant concentration had no effect on the size and size distribution of both pure gemini aggregrates, but after mixing with SDS, the size and size distribution of aggregates was changed with the total surfactant concentration in esterquat gemini. At lower concentration (i.e, 5 mM), the presence of SDS causes less repulsive electrostatic interaction between head groups of esterquat gemini and growing the micelles. At higher concentration (i.e, 15 mM), when esterquat gemini concentration is in excess compared to SDS, some esterquat gemini surfactants tend to aggregate themselves. Thus, two size distributions were observed: one of gemini-rich micelles around 2.4 nm, and the other larger of aggregates (23 nm) resulting from entering SDS molecules to esterquat gemini micelles. Table 5 shows that the aggregate size and size distribution of betainate gemini at both concentrations did not noticeably change upon mixing with SDS. This indicates that the synergism between betainate gemini and SDS was little, as shown in the previous section. There was a considerable reduction in zeta potential of esterquat gemini after mixing with SDS, but the zeta potential of betainate gemini did not change a lot after mixing with SDS, showing a little entrance of SDS into the mixed micelles. These results were in good agreement with the surface tension data, showing the strong synergism between esterquat gemini and SDS while a weak synergism between betainate gemini and SDS.

Figure 3 shows the TEM imaging of pure gemini surfactants and mixed systems in the absence of KCl. As can be seen, pure esterquat and betainate geminis formed spherical micelles, and the morphology of these geminis did not change upon mixing with SDS. The micelles of esterquat gemini were grown after mixing with SDS, but the micelle size of betainate gemini did not change upon mixing with SDS. The results of TEM imaging were consistent with the DLS size data.

(b). In the Presence of KCl. CV measurements were done to determine the diffusion coefficients of pure and mixed aggregates and the interparticle interaction parameters.[48] The micellar self-diffusion (Table 1, eq 16) was obtained from the cyclic voltammograms for one electron oxidation of ferrocene, which is assumed to be completely solubilized in the micellar phase. Ferrocene can be used, provided that it does not perturb the micelle.[33] The electrochemistry of ferrocene in nonaqueous, aqueous, and micellar environments is described elsewhere.[49,50]

The dependence of the self-diffusion coefficient on surfactant concentration is shown in Figure 4. For pure esterquat and

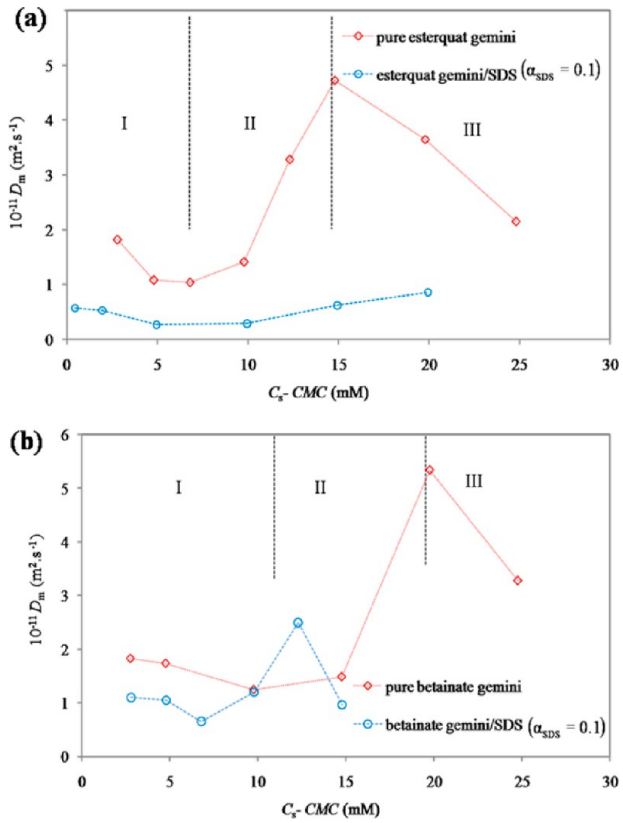


Figure 4. Diffusion coefficient versus surfactant concentration in the presence of 0.05 M KCl at 298 K.

betainate geminis, the corresponding plots consist of three separate regions. First, the diffusion coefficient decreased linearly as concentration rises (region I), which is attributed to a micelle size growth or intermicellar interaction without any micellar transformation. The considerable increase in diffusion coefficient in the region II implies that a phase transition from larger particles (region I) to smaller ones (region III) occurred, which was proved by TEM images.

Figure 5a,c shows that esterquat and betainate geminis formed cubic nanoparticles (or cobosomes) and vesicles at region I, respectively. These structures transformed to micelles at region III (Figure 4). In region III, D_{agg} was decreased again due to interparticle interaction between micelles. Such micellar transitions for catanionic surfactant systems have been reported by our group[33,51] and other researchers.[52,53] Cobosomes are formed when the packing parameter (for definition see Supporting Information) is more than unity and it has been also reported for some systems in the literatures.[54−58] The preparation of cobosomes is usually achieved by high pressure homogenization or ultrasonication of the viscous bulk phase.[59] Here, esterquat gemini spontaneously formed cobosomes in the presence of KCl, which is the importance of the current study. A common application for such new aggregates is as drug delivery vehicles.[60] The vesicle-to micelle transition is of

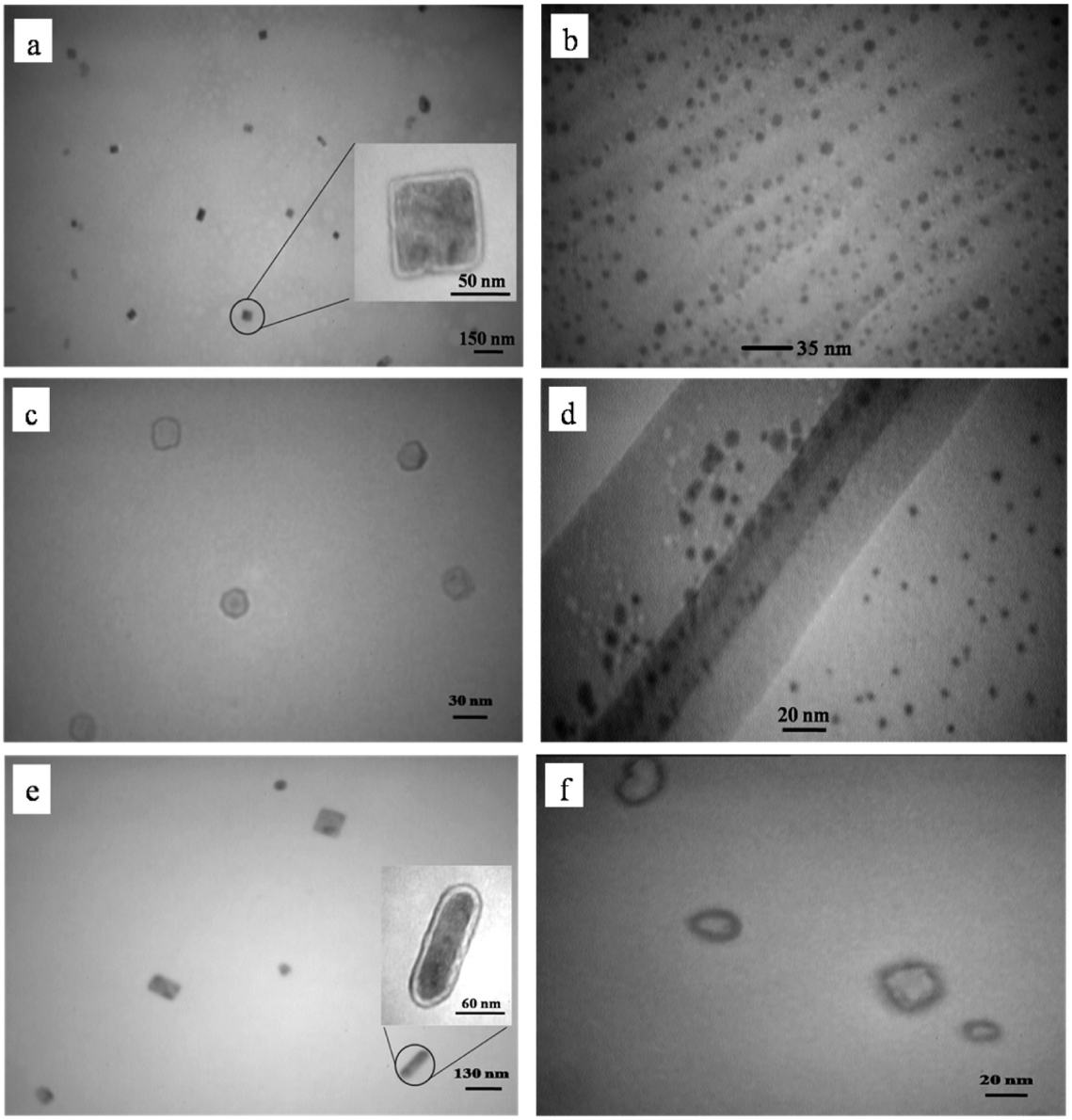


Figure 5. TEM images in the presence of 0.05 M KCl: (a) pure esterquat gemini (5 mM), (b) pure esterquat gemini (15 mM), (c) pure betainate gemini (7 mM), (d) pure betainate gemini (20 mM), (e) esterquat gemini/SDS (α_{SDS} = 0.1) at C_{tot} = 5 mM, and (f) betainate gemini/SDS (α_{SDS} = 0.1) at C_{tot} = 5 mM.

significant interest because the more highly ordered vesicle structure spontaneously transforms into a less highly ordered micelle structure with increase in the surfactant concentration, which is completely opposite to the general theory regarding the self-assembly of surfactants.[61] Recently, vesicle-to-micelle transition in single surfactant systems has been reported; where the surfactants are single tailed and have weakly acidic carboxylate or phosphate headgroups.[61,62]

The D_{agg} for esterquat gemini/SDS system first decreased and then began to increase. A small increase in diffusion coefficient in the region II implies that a size change in micellar aggregates took place. DLS size measurements for esterquat gemini/SDS system at 5 mM and 15 mM (Table 6) also revealed the change in size of aggregates. In the betainate gemini/SDS system, the corresponding plot consists of three separate regions like pure betainate gemini (Figure 4b). However, it seems the morphology change occurred at lower concentrations compared to pure betainate gemini. DLS size measurements (Table 6) showed that no significant difference in aggregate size was observed for betainate gemini/SDS system at 5 mM and 15 mM. For esterquat gemini/SDS system, the values of D_{agg} at all concentrations were smaller than those of pure esterquat gemini, which indicates that the larger aggregates were formed in esterquat gemini/SDS.

Figure 5e,f shows the corresponding TEM imaging for the mixed gemini-SDS systems in the presence of KCl. Upon mixing with SDS (α_{SDS} = 0.1), the morphology of esterquat gemini changed from cubic nanoparticles (or cobosomes) to elongated and cylindrical nanoparticles coexistent with cobosomes (Figure 5e). However, the betainate gemini vesicular structures remained spherical, and no dramatic structural changes took place in the solution upon mixing with SDS (Figure 5f).

The mean diameters of aggregates obtained by three different methods (i.e., CV, DLS and TEM) are summarized in Table 6. The viscosities of solutions for calculating hydrodynamic radius

Table 6. The Mean Diameter of Aggregates Obtained by DLS, CV, and TEM in the Presence of 0.05 M KCl and at 298 K

$[C_{tot}]$ (mM)	system	Mean diameter (nm)		
		DLS	CV	TEM
5	esterquat gemini	28.76	31.1	40−50
15	esterquat gemini	2.01	7.2	3−9
		7.51		
5	betainate gemini	24.36	22.8	20−25
20	betainate gemini	4.19	3.1	4−8
5	esterquat gemini/SDS (α_{SDS} = 0.1)	56.41[a]	124.1[a]	cylinder (60 × 120)
15	esterquat gemini/SDS (α_{SDS} = 0.1)	28.31	36.5	-
5	betainate gemini/SDS (α_{SDS} = 0.1)	30.28	34.0	25
15	betainate gemini/SDS (α_{SDS} = 0.1)	25.73	21.7	-

[a]The size of aggregates could not measured accurately because of cylindrical shape of aggregates.

are given in the Supporting Information. It should be noted that all values reported in Table 6 are the average size of aggregates, and there is a good agreement between the values given by three mentioned methods. As can be seen from Table 6, the mean diameter of esterquat gemini at 5 mM, obtained from DLS, was around 28.76 nm and it was changed to 2.01 and 7.51 nm at 15 mM, showing that large aggregates changed to small micelles as indicated by CV measurement. The mean diameter of betainate gemini at 5 mM was also around 24.36 nm, and it was changed to 4.19 nm at 20 mM, confirming the phase transition predicted by CV measurement. Table 6 also shows that the size of esterquat gemini aggregates upon mixing with SDS changed a lot, while no noticeable change in betainate gemini aggregate size was observed after mixing with SDS.

Applying eq 17 (Table 1) in region I, k_d was directly obtained from the curve by dividing the slope by the intercept. The k_d and D^0_{agg} values are listed in Table 7. According to Table 7,

Table 7. Values of k_d and D^0_{agg} Obtained by CV Measurement

system	k_d (mM^{-1})	$D^0_{agg} \times 10^{-11}$(m^2·s^{-1})
esterquat gemini	0.084	2.31
betainate gemini	0.040	2.09
esterquat gemini/SDS (α_{SDS} = 0.1)	0.136	0.65
betainate gemini/SDS (α_{SDS} = 0.1)	0.073	1.47

addition of SDS to esterquet gemini solution resulted in a notable increase in aggregate size (or decrease D^0_{agg}) and interparticle interaction parameter (k_d). The efficiency of oppositely charged SDS molecules in reducing electrostatic repulsion between esterquet gemini head groups is the main cause of increase in aggregate size, which consequently results in the formation of the elongated and cylindrical liquid crystalline phases. The variation in k_d can be interpreted from the viewpoints of aggregate's surface charge density and phase transition/micellar growth.[50] The unexpected increase in k_d values, in spite of the decrease in micellar surface charge density with addition of SDS, can be mainly attributed to morphology change. No significant change in k_d and D^0_{agg} could be observed for betainate gemini upon mixing with SDS. These results were in agreement with TEM characterization indicating no change in betainate gemini aggregate shape (Figure 5c,f). The betainate gemini at 5 mM formed vesicles at mean diameter around 20−25 nm and the same size obtained for vesicles in betainate gemini/SDS system. In addition, the X_1 value (Table 2) obtained from tensiometry validated the finding that the SDS monomers do not have a high tendency to enter the betainate gemini aggregates.

The results showed that the presence of KCl as electrolyte had considerable effect on size and morphology of these geminis. It can be concluded that the packing parameter increased with increasing ionic strength, which can be attributed to the reduction in cross-sectional area occupied by the hydrophilic portion at the micelle-solution interface due to the compression of the electrical double layer surrounding the ionic surfactant.[63,64] An increase in packing parameter may result in the formation of types of aggregates such as vesicles and cobosomes. In our previous work,[24] it was shown that these geminis formed small spherical micelles in pure solution and even in the presence of a low concentration of NaBr electrolyte. This indicates that the electrolyte should be used at high concentration to observe its effect on size and morphology of these geminis.

4. CONCLUSION

The results showed that the position of ester bonds in alkyl tail plays an important role in both physicochemical properties and aggregation behavior of pure ester-containing gemini surfactants and their binary mixed system with SDS in the presence of KCl. The results also showed a phase transition from cubic nanoparticles and vesicles to small micelles as the surfactant concentration increase in presence of KCl for esterquat gemini and betainate gemini, respectively. The present investigation suggests a never before reported structural behavior of ester-containing gemini surfactant aggregates in which they transform from cubic nanoparticles to vesicles in the presence of electrolyte as the position of ester bond in alkyl chain is changed. Esterquat gemini (in the presence of 0.05 M KCl) formed cubic nanoparticles (or cobosomes) and its phase changed to cylindrical nanoparticles coexistent with cobosomes after mixing with SDS. Betainate gemini formed spherical vesicles and no noticeable structural changes was observed in solution after mixing with SDS. These results were in good agreement with the surface tension data, which showed a small synergism for betainate gemini/SDS and a high synergism for esterquat gemini/SDS system. Current study showed that these geminis, in the presence of additives, spontaneously formed cobosomes and vesicles in the nanometer range, which makes them potentially applicable as drug delivery vehicles.

■ ASSOCIATED CONTENT

Supporting Information

Description of equation symbols in Table 1, phase behavior of geminis at various mole fractions of SDS, DLS diagrams, a Table showing viscosity of solutions. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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