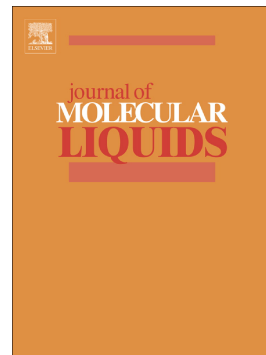# Accepted Manuscript

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Synthesis, surface activity and thermodynamic properties of cationic gemini surfactants with diester and rigid spacers

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Abstract A group of cationic gemini surfactants with diester and rigid spacers, 12-Ph-12, 14-Ph-14, 16-Ph-16, were synthesized and confirmed by IR, ^{1}H NMR and elemental analysis. The surface parameters of the synthesized gemini surfactants including: the critical micelle concentration (CMC), the surface tension value at CMC (γ_{CMC}), effectiveness (π_{CMC}), efficiency (pC_{20}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}), were obtained from surface tension measurements. These gemini surfactants showed higher surface activity than the traditional monomeric surfactants. The thermodynamic parameters of micellization process from conductivity measurements showed that the micellization was a spontaneous and exothermic process in environment, and the micellization process becomes less favorable with the decrease of alkyl chain length and increase in temperature. The micropolarity was evaluated from steady fluorescence spectra, and the dye solubilization was investigated by using UV-visible spectroscopy. The results revealed that the micropolarity of surfactant micelles is very low and these gemini surfactants can really enhance the solubility of water insoluble dyes.

Keywords Gemini surfactants, Diester and rigid spacers, Surface activity properties, Thermodynamic parameters, Dye solubilization

1. Introduction

Gemini surfactants represent a novel class of surfactants, which are made up of two conventional monomeric surfactant units linked by a flexible or rigid spacer at or very close to the head groups. It has been found that gemini surfactants can exhibit superior solution properties compared to the corresponding single-chained surfactants in many aspects, such as lower critical micelle concentration (CMC), more efficient in lowering the surface tension of water, better emulsifying properties and unusual aggregation morphologies [1-5]. Owing to their unique performance, the use of gemini surfactants covers the substantial homogeneous catalytic reactions along with solubilisation, emulsification, and many more technical applications in industries such as industrial detergency, gene transfection, micellar catalysis and corrosion inhibitors [6-9].

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In recent years, there has been a particular interest in gemini surfactants with rigid spacers, partly because they possess particular performance and broad application prospects [10-16]. Xie et al. [15] reported two novel carboxylate gemini surfactants with a long and rigid spacer, and found that the gemini surfactants containing rigid group spacer could form large size aggregation and spherical micelles in aqueous solution. Zhu et al. [16] synthesized four anionic gemini surfactants with long rigid or semi-rigid spacers and investigated their surface and aggregation properties in water, all the gemini surfactants possessed high surface activities and excellent micelle forming ability. Obviously, the existence of a rigid spacer plays an important role in the properties of gemini surfactants.

Enlightened by the advantages of inserting the rigid spacers in the structure of gemini surfactants, herein in this paper, we designed and synthesized a series of cationic gemini surfactants with diester and rigid spacers (Scheme 1). The diester group was also introduced to the spacers of our gemini surfactants with the expectation that the properties of gemini surfactants can be further improved. The surface tension, thermodynamic properties of micellization and micropolarity for the gemini surfactants, which are essential for the prediction of applications, have been measured by tensiometry, conductometry and steady-state fluorescence. Moreover, the effect of different concentrations of gemini surfactants on the dye solubilization was also investigated by using UV-visible spectroscopy.
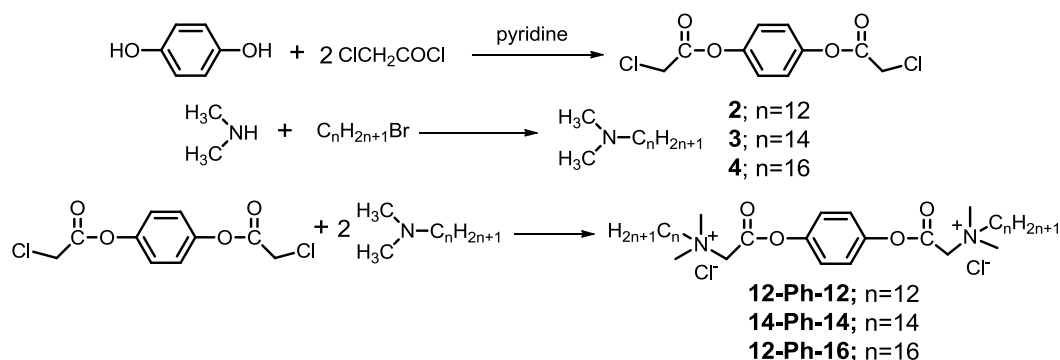
Scheme 1. Synthetic routes for the gemini surfactants.

2. Experimental Section

2.1 Materials

1-bromododecane (>98%), 1-bromotetradecane (>98%), 1-bromohexadecane (>98%), acetone, dimethylamine (33% aqueous solution), chloroacetyl chloride (≥98%), ethyl acetate, ethanol were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). Pyrene, Methyl red and Hydroquinone (>98%) were purchased from Sigma-Aldrich and used as received without further purification. Ultrapure water was used in all experiments.

^{1}H NMR spectra were recorded on a Bruker AV 400 NMR Spectrometer (Bruker Corporation, Switzerland, 400 MHz). Elemental analyses were carried out on a vario EL III Element Analyzer (Elementer Corporation, Germany). The infrared (IR) spectra were measured on a Japan FT/IR-430 spectrometer as KBr pallets.

2.1.1 Synthesis of 1,4-phenylene bis(2-chloroacetate) (1)

Chloracetyl chloride (0.21 mol, 23.73 g) was slowly added to a stirred solution of hydroquinone (0.11 mol, 11.57 g) and pyridine (0.21 mol, 16.62 g) in 100 mL dichloromethane at 0 ℃. Then, the reaction mixture was stirred for 3 h at 40 ℃ and neutralized to a pH = 7 with saturated sodium bicarbonate solution. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum and the residue was recrystallized from a mixture solution of acetone and petroleum (3:1) to give compound 1 as white crystals (24.87 g, 93.13% yield based on hydroquinone). ^{1}H NMR (400 MHz CDCl$_3$, TMS) δ ppm: 4.30 (s, 4H), 7.16 (s, 4H); IR (KBr) cm^{-1}: 3033, 2953, 1761, 1507, 1410, 1312, 942, 861, 814, 737, 684, 528;

2.1.2 Synthesis of compounds 2-4

A mixture of 1-bromoalkane (0.10 mol) and dimethylamine (33% aqueous solution, 0.50 mol, 5 equiv) in ethanol (40 mL) was added to a dried 100 mL 2-necked flask. The solution was heated at 80 ℃ for 24 h. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum, and the residue was poured into the saturated sodium bicarbonate solution (60 mL). The mixture was extracted with ethyl acetate, and the extract phase was dried with anhydrous magnesium sulfate. The solvent was removed by distillation under reduced pressure and the solid residue was purified by distillation to give compounds 2-4 as colorless oily products.

N,N-Dimethyldodecylamine (2, 20.15 g, 93.62% yield based on 1-bromododecane). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ ppm: 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.28-1.26 (d, J = 8.0 Hz, 18H), 1.47 (s, 2H), 2.23-2.30 (m, 8H); IR (KBr) cm^{-1}: 2925, 2854, 1464, 721.

N,N-Dimethyltetradecylamine (3, 22.10 g, 91.08% yield based on 1-bromotetradecane). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ ppm: 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.26 (s, 22H), 1.47 (s, 2H), 2.23-2.30 (m, 8H); IR (KBr) cm^{-1}: 2924, 2853, 1465, 721.

N,N-Dimethylhexadecylamine (4, 24.24 g, 89.59% yield based on 1-bromohexadecane). ^{1}H NMR (400 MHz CDCl$_3$, TMS) δ ppm: 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.26 (s, 22H), 1.47 (s, 2H), 2.21-2.26 (m, 8H); IR (KBr) cm^{-1}: 2924, 2853, 1463, 720.

2.1.3 Synthesis of gemini surfactants

A solution of 1,4-phenylene bis(2-chloroacetate) (10.00 mmol) and N,N-dimethylalkylamine (44.00 mmol, 2.2 equiv) in ethyl acetate (40mL) was stirred and refluxed for 8 h. Upon cooling to room temperature, a white precipitate was formed. The precipitate was filtered and washed with plenty of ethyl acetate, then dried under reduced pressure. The crude product was recrystallized two times from acetone/acetonitrile (3:1) to afford the gemini surfactants as white crystals.

12-Ph-12 (5.86 g, 85.05 % yield based on 1,4-phenylene bis(2-chloroacetate)). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ ppm: 0.86-0.90 (t, J = 8.0 Hz, 6H), 1.25-1.36

(m, 36H), 1.83 (s, 4H), 3.65 (s, 12H), 3.85-3.91 (t, J = 8.0 Hz, 4H), 5.97 (s, 4H), 6.94 (s, 4H); IR (KBr) cm^{-1}: 2920, 2851, 1767, 1503, 1465, 1398, 1160, 1016, 988, 892; Anal. Calcd. for $C_{38}H_{70}O_4N_2Cl_2$ %: C, 66.16; H, 10.23; N, 4.06. Found %: C, 65.98; H, 10.28; N, 4.01.

14-Ph-14 (6.49 g, 87.11 % yield based on 1,4-phenylene bis(2-chloroacetate)). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ ppm: 0.86-0.90 (t, J = 8.0 Hz，6H), 1.25-1.36 (m, 44H), 1.83 (s, 4H), 3.65 (s, 12H), 3.85 (s, 4H), 5.95 (s, 4H), 6.87 (s, 4H); IR (KBr) cm^{-1}: 2920, 2850, 1767, 1504, 1465, 1399, 1158, 1016, 996, 892; Anal. Calcd. for $C_{42}H_{78}O_4N_2Cl_2$ %: C, 67.62; H, 10.54; N, 3.76. Found %: C, 67.04; H, 10.59; N, 3.71.

16-Ph-16 (7.11 g, 88.76 % yield based on 1,4-phenylene bis(2-chloroacetate)). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ ppm: 0.89-0.90 (t, J = 8.0 Hz，6H), 1.25-1.82 (m, 52H), 1.82 (s, 4H), 3.63 (s, 12H), 3.88 (s, 4H), 5.92 (s, 4H), 6.88 (s, 4H); IR (KBr) cm^{-1}: 2919, 2850, 1764, 1540, 1492, 1466, 1399, 1158, 1002, 983, 892; Anal. Calcd. for $C_{46}H_{86}O_4N_2Cl_2$ %: C, 68.88; H, 10.81; N, 3.49. Found %: C, 68.66; H, 10.86; N, 3.45.

2.2 Methods

2.2.1 Surface tension measurement

The surface tensions of the gemini surfactant solutions were measured with a Wilhelmy plate technique (Krüss K20 Tensiometer, Germany) [17] at 298.15 ± 0.1 K, and the surface tension values were measured at least three times. The surface tension of pure water was obtained as being 71.99 ± 0.05 mN/m at 298.15 K. All solutions were prepared with ultrapure water.

2.2.2 Electrical conductivity measurement

The conductivity measurements were made by using a direct reading conductometer, model S320 (Mettler-Toledo GmbH, Switzerland) at different temperatures, KCl solution (0.1 M and 0.01 M) was used for calibration of conductivity cell. The conductivity was recorded when its value fluctuated less than 1% over a 5 min interval. The tested solution was added to a container kept in a thermostat (THD 0506, NingBo TianHeng Instrument Factory, China) with the temperature accuracy of ± 0.01℃. The concentration at the break point of the curve of the conductivity *versus* concentration was the critical micelle concentration (CMC) of gemini surfactants [18].

2.2.3 Steady-state fluorescence measurement

Fluorescence measurements were performed using a F-4600 Fluorescence spectrophotometer (Hitachi High-Technologies Corp, Tokyo Japan). Pyrene was used as the fluorescence probe to investigate the micropolarity of gemini surfactant solutions. The excitation wavelength was 336 nm, the emission spectra were scanned over the spectrum range of 345-460 nm, and the slit widths of excitation and emission were fixed at 5.0 and 2.5 nm, respectively. The ratio of the intensities of the first peak (around 373 nm) to the third peak (around 384 nm) was used as an index of the

polarity of the pyrene-solubilizing medium (I_1/I_3) [19]. All solutions were prepared by injecting the appropriate amount of ethanolic pyrene solution (1×10^{-3} M, 0.1 % of the volume of the gemini surfactants solution) into the gemini surfactant solution, followed by ultrasonication at 298.15 K for 2 h.

2.2.4 Dye solubilization measurements

Batch tests for solubilization of methyl red (a water insoluble dye was used) in various concentrations of gemini surfactant aqueous solutions were performed. Excess amounts of methyl red were added to different concentration gemini surfactant solutions which were stirred for 24 h at 298.15 K. Nondissolved methyl red was filtered through 0.45 μm PVDF filters and the concentration of dissolved methyl red was determined from absorption measurements at 520 nm (pH = 7) using a Shimadzu UV-3600 spectrophotometer. A reference blank was prepared of the same surfactant concentration to eliminate the effect of surfactant on UV absorbance. All measurements were performed in triplicate and UV spectra of the methyl red in gemini surfactant solutions were recorded in the wavelength range 250-600 nm.

3. Results and discussion

3.1 Synthesis

The general synthetic procedures for cationic gemini surfactants with diester and rigid spacers (**12-Ph-12**, **14-Ph-14**, **16-Ph-16**) are outlined in Scheme 1. They were easily prepared following the three-step procedure from the starting materials. First, the commercially available hydroquinone was reacted with chloracetyl chloride in the presence of pyridine to afford the key intermediate 1,4-phenylene bis(2-chloroacetate) (**1**). Then alkylation of 1-bromoalkane (1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, 1 equiv) with an excess molar ratio of dimethylamine (5 equiv) generated compounds **2**, **3**, and **4**. Finally the gemini surfactants **12-Ph-12**, **14-Ph-14** and **16-Ph-16** were prepared at a high yield of 85.05-88.76 % by quaternization of 1,4-phenylene bis(2-chloroacetate) (**1**) with *N,N*-dimethylalkylamine (**2**, **3**, **4**), respectively. The chemical structures of the synthesized gemini surfactants were unambiguously characterized by [^1]H NMR spectroscopy, infrared spectroscopy and elemental analysis.

3.2 Surface activity of the gemini surfactants

The surface tension (γ) versus logarithm of concentration (C) profiles for the gemini surfactant aqueous solutions were obtained at 298.15 K. As shown in Fig. 1, the surface tension value decrease initially with the increase of gemini surfactants concentration at the lower ranges and then achieve a relative stable value at higher concentrations. The concentration at the break point is usually described as the CMC of a gemini surfactant. The surface activity parameters of the gemini surfactants are summarized in Table 1. The CMC values of **12-Ph-12**, **14-Ph-14** and **16-Ph-16** are 1.107, 0.2965 and 0.05530 mmol/L at 298.15 K, respectively, indicating excellent micelle forming ability. Evidently, the CMC value gradually decreased with

increasing number of carbon atoms of the alkyl chains from 12 to 16, which was often observed in common ionic surfactants with a homologous compound. In comparison with the traditional monomeric surfactants CTAB (hexadecyltrimethylammonium bromide) and DTAB (dodecyltrimethylammonium bromide) under the same conditions, the CMC values for these gemini surfactants are much lower than traditional monomeric surfactants with the same hydrophobic chain. It demonstrated that the surface activity of synthesized cationic gemini surfactants is superior to that of traditional monomeric surfactants.

The important physicochemical parameters including the surface tension value at cmc (γ_{CMC}), the minimum surface area (A_{min}) occupied by the gemini surfactant molecule, and the surface excess concentration (Γ_{max}), are listed in Table 1 for each gemini surfactant. The surface area (A_{min}) occupied by the gemini surfactant molecules at the air-water interface reflect their packing density [20]. The surface excess concentration (Γ_{max}) and the area occupied by a surfactant molecule (A_{min}) at the air-water interface were calculated by the Gibbs adsorption Equation (1) and (2) [21,22]:

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

$$A_{min} = \frac{10^{16}}{N_{A}\Gamma_{max}} \qquad (2)$$

Where R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), C is the concentration of gemini surfactant (mol/L), $d\gamma/d\log C$ is the slope below the CMC in the surface tension vs. concentration curves, N_A is Avogadro's number (6.02×10^{23} mol^{-1}). The values of n = 3 (the number of species at the interface whose concentration changes with the surfactant concentration) are used for calculating the Γ_{max} values [23,24]. As shown in Table1, the Γ_{max} values of these gemini surfactants decrease, but the A_{min} values increase with the increase of the hydrocarbon chain from 12 to 16, which suggest the gemini surfactant with the longer hydrophobic chain has lower packing densities at the air-water interface. The possible explanation is that the longer hydrophobic chain is more prone to bend at the air/water interface [25].

From the surface tension curves, two other important parameters, the adsorption efficiency (pC_{20}) and the effectiveness of surface tension reduction (π_{CMC}) can be also obtained in Table 1. The former parameter is calculated by using the Equation (3):

$$pC_{20} = -\log C_{20} \qquad (3)$$

Where C is the molar concentration of gemini surfactant (mol/L) and C_{20} stands for the surfactant concentration required to reduce the surface tension of pure water by 20 mN/m. The pC_{20} value reflects the adsorption efficiency of surfactant molecules at the air-water interface, the greater the pC_{20} value is, the more efficient the surfactant molecule adsorbs at the air-water interface. The other parameter, π_{CMC} is the surface pressure at CMC, which is defined as the following Equation (4):

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \qquad\qquad (4)$$

Where γ_0 and γ_{CMC} are the surface tension of water and the surfactant solution at CMC, respectively. π_{CMC} represents the maximum reduction of surface tension caused by the dissolution of surfactant molecules, becomes an indication for the effectiveness of gemini surfactant to reduce the surface tension of water [20]. Hence, the larger the π_{CMC} value is, the higher the effectiveness of gemini surfactant is. From the values of pC_{20} and π_{CMC} in Table 1, the pC_{20} values of the gemini surfactants are 3.20, 3.62 and 4.26 at 298.15 K, respectively. It is clear that the adsorption efficiency increases with increasing length of the hydrophobic chain. The π_{CMC} values of each gemini surfactants are 39.68, 36.99 and 35.51 at 298.15 K, respectively, which indicate that the π_{CMC} value decreases with increasing alkyl chain length.

In addition, the value of CMC/C_{20} ratio can be taken as a measure of structural factors in the adsorption and micellization process. The gemini surfactant with lower CMC/C_{20} ratio has greater tendency to form micelles than to adsorb at the interface in aqueous solution. As shown in Table 1, it is clear that the gemini surfactants with longer hydrophobic chain length were easier to self-assemble than adsorb at the air-water interface in aqueous solution. The γ_{CMC} values of the gemini surfactants are 32.29, 34.98 and 36.46 mN/m at 298.15 K, respectively. The results show that the γ_{CMC} values increased from 32.29 to 36.46 mN/m with increasing hydrophobic chain from 12 to 16.
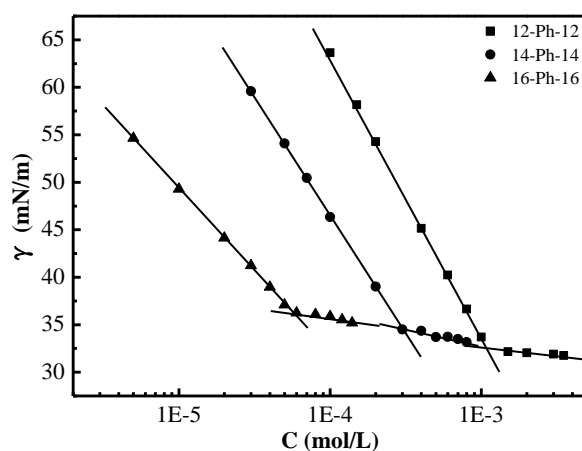

Fig. 1. Surface tension (γ) vs the concentration (C) plots for the gemini surfactants at 298.15 K.

Table 1

Surface active properties and parameters of the gemini surfactants at 298.15 K.

Compounds	CMC[a] (mM)	CMC[b] (mM)	γ_{CMC} (mN/m)	Γ_{max} (μmol/m^2)	A_{min} (nm^2)	pC_{20}	π_{CMC} (mN/m)	CMC/C_{20}
12-Ph-12	1.107 ± 0.04	1.215 ± 0.02	32.29	1.74	0.96	3.20	39.68	1.75
14-Ph-14	0.2965 ± 0.02	0.3097 ± 0.01	34.98	1.44	0.12	3.62	36.99	1.24
16-Ph-16	0.05530 ± 0.005	0.06840 ± 0.004	36.46	1.02	1.63	4.26	35.51	1.01

[a]Measured by tensiometry, [b]Measured by conductometry

3.3 Thermodynamic properties of micellization

In order to investigate the micellar behavior of the gemini surfactants in aqueous solution, the thermodynamic properties of micellization have been investigated by electrical conductivity measurements at four different temperatures (298.15, 303.15, 308.15 and 313.15 K). As shown in Fig. 2, the CMC values were determined as the sharp break points in the plots of specific conductance (κ) versus gemini surfactants concentration (C) [18], and the degree of counterion dissociation (α) was determined from the ratio of the pre-micellar slope ($S_1 = d\kappa/dC$) to the post-micellar slope ($S_2 = d\kappa/dC$), $\alpha = S_2/S_1$ [26,27]. The values of CMC for each gemini surfactants measured by the electrical conductivity measurement are 1.215, 0.3097 and 0.06840 mmol/L at 298.15 K, respectively, which are close to the CMC values measured by surface tension measurements. The data in Table 2 show that the CMC values increase with the temperature. This character is in agreement with that of the other typical ionic surfactants. In addition, the α values decrease significantly with increasing hydrophobic tail length for the gemini surfactants. The long hydrophobic tails favor to form micelles and result in a decrease in CMC values.

The standard Gibbs free energy of the aggregation (ΔG^o_{mic}) can be calculated by the following equation (5) [28]:

$$\Delta G^o_{mic} = RT(3 - 2\alpha)\ln X_{CMC} \tag{5}$$

Where X_{CMC} is the CMC in mole fraction, R is the gas constant and T is temperature on the Kelvin scale, respectively. The X_{CMC} is calculated by using the equation of $X_{CMC} = $ CMC /(CMC + number of moles for the solvent).

As shown in Table 2, the calculated negative values indicate that the micellization is a spontaneous process and the ΔG^o_{mic} of the investigated gemini surfactants have been found to be hydrophobically driven force for the formation of micelles increases with respect to increasing alkyl chain length, which leads to the most negative of ΔG^o_{mic} value for **16-Ph-16**. On increasing the temperature from 298.15 K to 313.15 K, the absolute values of ΔG^o_{mic} are increased due to the lower stability of the micellized gemini surfactant molecules than the reely dispersed molecules in the aqueous phase. The standard enthalpy change for micellization process (ΔH^o_{mic}) can be determined using the Gibbs-Helmholtz equation (6) [28]:

$$\Delta H^o_{mic} = -RT^2(3 - 2\alpha)\left(\frac{\delta \ln X_{CMC}}{\delta T}\right)_P \tag{6}$$

The values of $\ln x_{cmc}$ in aqueous solutions were plotted against the temperature and the slopes of these plots were taken as the values of $d\ln X_{CMC}/dT$. The calculated ΔH^o_{mic} values at four temperatures in aqueous solutions are listed in Table 2. The values of standard enthalpy of micellization (ΔH^o_{mic}) are negative for all the systems studied. It means that the micellization process is exothermic in aqueous solutions. The negative value of the ΔH^o_{mic} is mostly becoming more negative with increase in alkyl chain length of the gemini surfactants. It means that, the micellization process in **16-Ph-16** is more exothermic than **14-Ph-14** and **12-Ph-12** at the same temperature. Furthermore, The standard entropy of micelle formation (ΔS^o_m) can be calculated by

8

the following equation (7) [28] and the values are summarized in Table 2.

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

From the observed data, one can see that the ΔS^{o}_{mic} values are positive in all cases, suggesting that the entropy change is favorable to the formation of the micelles. The ΔS^{o}_{mic} tends to be less positive with the increasing temperature in range from 298.15 K to 313.15 K in aqueous solutions for the gemini surfactants, because the surrounding iceberg structures of surfactant molecules diminished in size or became less rigid as temperature increased. Thus the formation of micelles is difficult at higher temperature.
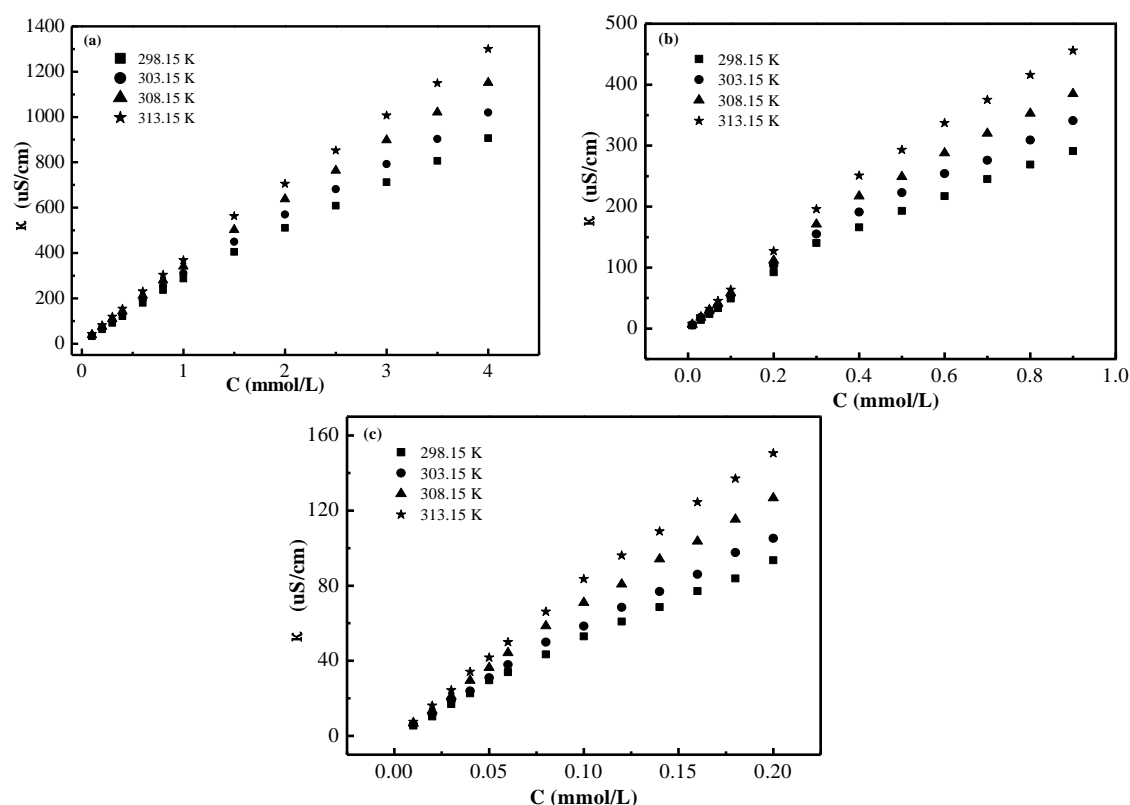

Fig. 2. Electrical conductivity (κ) versus the concentration (C) for (a) **12-Ph-12**, (b) **14-Ph-14** and (c) **16-Ph-16** at various temperatures.

Table 2
Thermodynamic parameters for micellization of gemini surfactants in aqueous solutions at various temperatures (T).

Compounds	T/K	CMC (mM)	α	ΔG^{o}_{mic} (kJ/mol)	ΔH^{o}_{mic} (kJ/mol)	ΔS^{o}_{mic} (kJ/K/mol)
12-Ph-12	298.15	1.215 ± 0.02	0.7034	-42.34	-15.72	0.1948
	303.15	1.324 ± 0.02	0.7368	-40.90	-15.57	0.1863
	308.15	1.397 ± 0.02	0.7666	-39.79	-15.46	0.1793
	313.15	1.498 ± 0.02	0.8004	-38.38	-15.23	0.1712
14-Ph-14	298.15	0.3097 ± 0.01	0.5421	-57.40	-24.90	0.2629
	303.15	0.3364 ± 0.01	0.5763	-55.88	-25.45	0.2533

	308.15	0.3604 ± 0.01	0.6019	-54.96	-25.08	0.2465
	313.15	0.3991 ± 0.01	0.6404	-53.08	-24.44	0.2358
16-Ph-16	298.15	0.06840 ± 0.004	0.6931	-54.39	-28.70	0.2787
	303.15	0.07690 ± 0.004	0.7236	-52.74	-28.55	0.2681
	308.15	0.08330 ± 0.004	0.7477	-51.68	-28.58	0.2605
	313.15	0.10190 ± 0.004	0.798	-48.34	-27.54	0.2423

3.4 Micropolarity

Fluorescence measurement is often employed to monitor the self-aggregation for gemini surfactant in aqueous solution by using the emission of pyrene [3,29,30]. The shape and intensity of the photoluminescence (PL) spectra for pyene is sensitive to its microenvironment at the site of solubilization of the fluorophore. Once the gemini surfactants begin to form micelles in aqueous solutions, the extreme hydrophobic pyrene molecules are transferred from the water environment to the hydrophobic core of micelles. Therefore, the fluorescence intensity ratio of the first to third band (I_1/I_3) is commonly used to analyze the micropolarity of the micelle system in polar media, reflecting the compactness of aggregates. Fig. 3 shows the variations of the pyrene polarity ratio I_1/I_3 with the change of the surfactant concentration. With increasing the gemini surfactant concentration close to the CMC value, there is an obvious decrease in I_1/I_3. Then the I_1/I_3 value keeps constant as the concentration of surfactant increases in aqueous solutions, which indicate that the aggregate structures are compact and the microenvironment does not change. Moreover, the final I_1/I_3 ratio for all three gemini surfactants is almost the same values as that of a conventional anionic surfactant, which indicates that the micropolarity of surfactant micelles is very low.
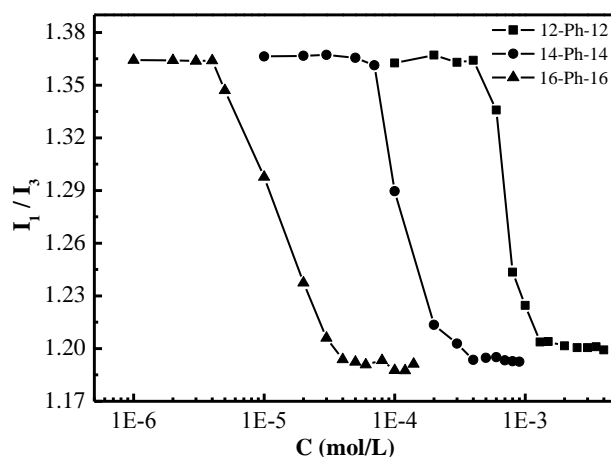

Fig. 3. Variation of the pyrene intensity ratio I_1/I_3 *vs* the concentrations (C) for the gemini surfactants at 298.15 K.

3.5 Dye solubilization

Dye solubilization of methyl red in various concentrations of gemini surfactant aqueous solutions were performed by using the UV-visible spectroscopy. As shown by the correlation of absorbance of methyl red at 520 nm in various concentrations of gemini surfactant aqueous solutions in Fig. 4, the absorbance of methyl red at 520 nm

increases with increasing the gemini surfactant concentration, which can be attributed to the increased solubility of methyl red in aqueous solutions. The absorbance of methyl red increases rapidly when the gemini surfactant concentration reaches the CMC, and finally achieves a relatively stable value as the concentration of surfactant increases in aqueous solutions. In addition, the dye solubilization rate of methyl red for all three gemini surfactants decrease with increasing length of the hydrocarbon chains, indicating that hydrophobic tail length has a certain effect on the microenvironment. Based on the solubilization experiments, these gemini surfactants can really enhance the solubility of water insoluble dyes, which may further extend the potential application of dyes.
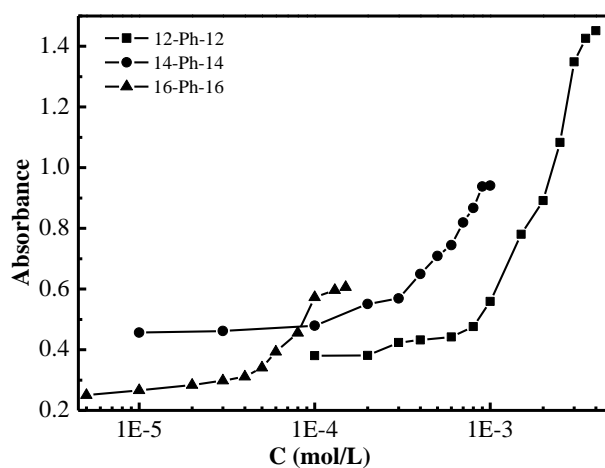

Fig. 4. Plot showing correlation of absorbance of methyl red in various concentrations of gemini surfactant aqueous solutions (at λ_{max} = 520 nm) at 298.15 K.

4. Conclusions

The physicochemical properties of three cationic gemini surfactants with diester and rigid spacers in aqueous solutions have been investigated. The surface activity of gemini surfactants increases with increasing the hydrophobic part: the γ_{CMC} values increased from 32.29 to 36.46 mN/m with increasing hydrophobic chain from 12 to 16. All the evaluated thermodynamic parameters show that the process of micellization is spontaneous and exothermic in environment, and the micellization process becomes less favorable with the decrease of alkyl chain length and increase in temperature. These investigated micellar systems show low micropolarity of surfactant micelles and solubilizing power toward hydrophobic compounds.

Acknowledgments

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Highlights

- A group of cationic gemini surfactants with diester and rigid spacers were synthesized and characterized
- The surface activity and thermodynamic properties of the micellization of gemini surfactants were investigated.
- The dye solubilization power of gemini surfactants was investigated by using UV-visible spectroscopy