



Gemini surfactants with short linkers: thermodynamics of Micelle formation

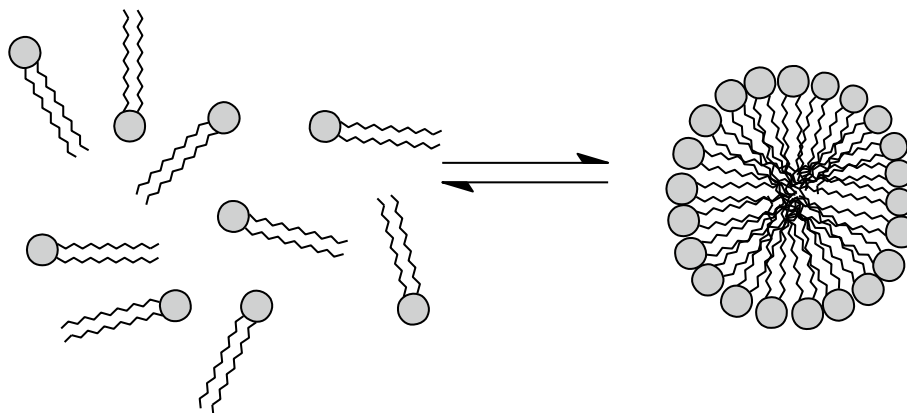
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Abstract

We have been investigating the physical properties of simple Gemini surfactant with short linker chains using conductivity, dynamic light scattering (DLS) and isothermal titration calorimetry (ITC). The surfactants used here have the general formula $(\text{CH}_3(\text{CH}_2)_{11})(\text{CH}_3)_2\text{-N}^+(\text{CH}_2)_n\text{-N}^+(\text{CH}_3(\text{CH}_2)_{11})(\text{CH}_3)_2\text{Br}_2$, where $n=2, 3$ or 4 and, as such, are designated as 12-2-12, 12-3-12 and 12-4-12. The ultimate goal of this work was to determine the enthalpy of demicellization using ITC. To determine the proper experimental conditions, it was necessary to first determine the critical micelle concentration (cmc) using conductivity and the size of the formed micelles using DLS for each surfactant. The results indicate a number of linear relationships between the number of carbons in the linker and certain physical properties such as cmc and ΔG_{mic} as determined by conductivity studies. As expected, demicellization is enthalpically unfavorable but entropically driven. Linear relationships are also observed between the number of linker carbons and some thermodynamic properties as determined by ITC.

Graphical abstract



Keywords Surfactants · Micelles · DLS · ITC · Thermodynamics

Introduction

The potential uses and applications of Gemini surfactants lie in their unique physical properties, most notably their low *cmc*s (critical micelle concentrations), good wettabilities and surface tension lowering properties. Potential applications include oil spill remediation agents [1], anti-corrosives [2, 3], antimicrobial and anti-algal agents [3–6] and gene therapy [8] to name a few. The major features governing the

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physical properties of a dicationic Gemini surfactant are: (1) the nature of the linker—composition and length [9–11]; (2) the nature of the head groups—composition, hydrophobicity, charge [13]; counterion [14]; and the length on the hydrophobic tails [11]. Each of these features contributes to the physical properties, and knowing these contributions, surfactants can be designed with fine-tuning of these properties for particular applications.

Like other surfactant molecules, Gemini surfactants self-assemble into micelles and/or other larger species. Further, the self-assembly is dependent upon the concentration of the surfactant. The hydrodynamic diameters (D_h), determined by dynamic light scattering (DLS) studies, of the formed micelles and the cmcs, determined by conductivity studies or other techniques, are important physical properties. For example, Li et al. described the properties of Gemini surfactants with a butyl linker, propyl head groups and tails of 10, 12, 14 and 16 carbons. They found that the cmc decreased with increasing tail length. Surfactants with tails of 10 and 12 carbons revealed two peaks in the DLS determination (2–3 nm and 10–100 nm) while the surfactants with 14 and 16 carbons reveal only one peak at 10–100 nm. The small radii species were attributed to individual micelles. Further analysis led to the conclusion that the large radii species (10–100 nm) were bilayered vesicles [13]. Garcia et al. investigated the influence of spacer hydrophilicity and flexibility on the aggregation behavior of Gemini surfactants. These surfactants had a variety of linkers and tails. Of particular interest to us, the 12-6-12 surfactant also displayed two peaks in the DLS determination—one at 2.29 nm (attributed to a spherical micelle) and one at 171.7 nm attributed to a micellar agglomerate [9].

Surfactants of general composition 14-s-14 (where $s = 3, 4, 5$ or 6 carbons in the linker, methyl head groups and tails of 14 carbons) were synthesized and characterized for micellar behavior. DLS studies of these surfactants indicated the presence of only micelles (1–10 nm) at the cmc, while increasing the concentration beyond the cmc leads to the formation of micellar agglomerates resulting in a second peak at 100–500 nm which increased in intensity with increasing concentration at the expense of the micelles [10]. The interplay between tail length and linker composition and length was also investigated by Parikh et al. DLS studies of the surfactants revealed only a single species for each (1.8–3.2 nm), and no peak for larger agglomerates was reported [11]. Finally, a recent study investigated the thermodynamics of micelle formation using both a Gemini surfactant and a zwitterionic surfactant. It was found that the structure of the Gemini surfactant played a significant role in the enthalpic and entropic contributions to the free energy of mixed micelle formations [15].

We were initially interested in determining the enthalpy of demicellization using isothermal titration calorimetry

(ITC) and simple Gemini surfactants with short linker chains ($n = 2, 3$ or 4), as shown in Fig. 1. For most of the literature reporting characterizations of Gemini surfactants, the surfactants had linkers of four or more atoms. Hence, the results reported here for the 12-2-12 and 12-3-12 surfactants are significant. We have also conducted conductivity and DLS measurements and report the results of these studies here.

Experimental

Materials

The Gemini surfactants (Fig. 1) were synthesized and purified as previously described [10]. Since these molecules have a saturated 12 carbon chain and linkers of 2, 3 or 4 methylenes, they will be referred to as 12-2-12, 12-3-12 or 12-4-12 surfactant. Surfactant solutions were prepared by dissolving the surfactant into ultra-pure $18.2 \text{ M}\Omega \text{ cm}^{-1}$ water.

Methodology

Conductivity studies

Conductivity measurements were determined with a Mettler Toledo SevenCompact Duo S213 Benchtop pH/Conductivity Meter with a standard micro conductivity probe. Solutions of each surfactant were prepared in ultra-pure water from 0 to 5 mM surfactant. Measurements were repeated until three consecutive identical readings were obtained.

Dynamic light scattering (DLS)

DLS measurements were performed with a Malvern Zeta-sizer μV DLS system equipped with a 633 nm He-NE laser and temperature control. To obtain a good signal, the surfactant concentrations for these studies were 15 mM. The data reported are the averages of at least 7 runs.

Isothermal titration calorimetry (ITC)

ITC experiments were carried out using a TA Instruments Nano ITC Standard volume model. The surfactant was

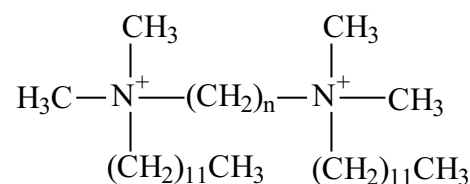


Fig. 1 Gemini surfactants studied here ($n = 2, 3$ or 4) as the dibromide

titrated into 300 μL of deionized and degassed water; 300 μL of the same water was placed in the reference cell for all experiments. For each titration, 50 μL of the surfactant at 15 mM was loaded into the injection syringe with the volume for each injection set at 2 μL every 3 min. The stir rate for each titration reaction was set at 300 rpm. The temperature for each titration ranged from 15–35 $^{\circ}\text{C}$. Each experiment was auto-equilibrated before titration began through the preset algorithm programmed by the TA software. The stir rate and injection time were calibrated to produce the least amount of instrument and experimental noise. The calibration of these variables was performed using water into water titrations, at varying temperatures from 15 to 55 $^{\circ}\text{C}$, stir rates from 200 to 400 rpm, injections intervals ranging from 1 to 5 min between injections and varying injection volumes from 1 to 3 μL . Thermodynamic parameters were determined by the TA NanoAnalyzeTM software.

Results and discussion

Figure 1 shows the general formula for the Gemini surfactants studied here. Each is characterized by having two quaternized ammoniums separated by a linker of 2 to 4 carbons. Each nitrogen also has two methyl groups and one dodecyl chain. The goal of this work was characterize these surfactants using conductivity, isothermal titration calorimetry (ITC) and light scattering (DLS) approaches.

Conductivity studies

The conductivity of an aqueous solution of surfactant is dependent upon, among other things, concentration of surfactant [9–11]. Figure 2 shows that the conductivities of surfactant solutions increase linearly with increasing concentration of surfactant but the slope of the conductivity/concentration linear regression line sharply breaks to one with a shallower slope at higher concentrations of surfactant. The break point is the critical micellization concentration or *cmc* and represents the initiation of micelle formation. Table 1 lists the determined values of *cmc* as determined by the Sheardy laboratory (RDS), the Bachofer laboratory (SB) and previously published values [16, 17, 24]. The *cmc* values reported in Table 1 are similar for all studies for the 12-2-12 and 12-3-12 surfactants; however, the *cmc* values for the 12-4-12 surfactant have some variability.

In a 1980 paper by Zana, the term α is defined as the degree of micelle ionization and can be determined by the ratio of the slope of the conductivity vs concentration above and below the *cmc* [19]. Later, in 1996, he used the value of β as the fraction of charges of micelle surfactant ions neutralized by the micelle bound monovalent counterions. He then derives the equation for the free energy of micelle

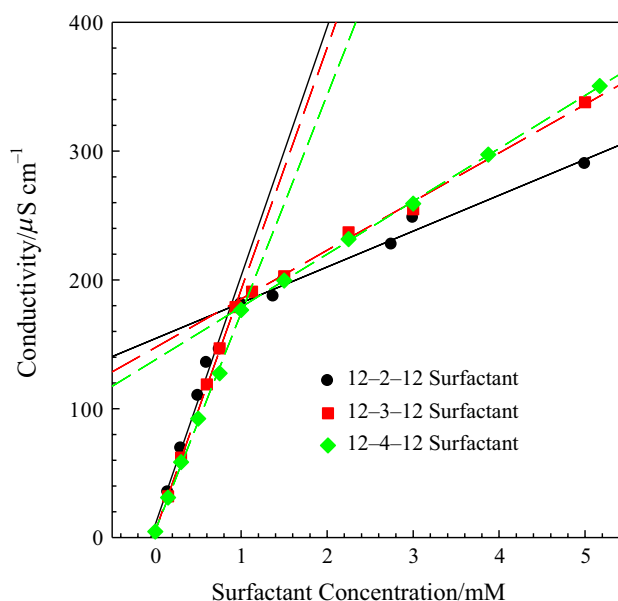


Fig. 2 Plots of conductivity as a function of surfactant concentration for the 12-2-12 (black circles, solid black regression line); 12-3-12 (red squares, medium dash red regression line) and 12-4-12 (green diamonds, short dash green regression line) surfactant. The regression lines represent the least squares linear regressions for the regions above and below the break points. These studies were carried out at 25 $^{\circ}\text{C}$ with the surfactant dissolved in ultra-pure water. (Colour figure online)

formation, ΔG_{mic} , for Gemini surfactants with monovalent counterions [20] where β is $1 - \alpha$ [13]

$$\Delta G_{\text{mic}} = RT(1/2 + b)\ln cmc - (RT/2)\ln 2 \quad (1)$$

Values of α and ΔG_{mic} determined here and by others are compared in Table 2. Also included in Table 2 are ΔG_{cal} as determined by isothermal titration calorimetry discussed below.

The plots in Fig. 3, using the RDS data, reveal linear relationships between number of carbons in the linker and *cmc*, α values or ΔG_{mic} . The decrease in ΔG_{mic} with increasing linker length is similar to previously published data [19, 20 and reference therein].

Dynamic light scattering studies

Solutions of the three surfactants in ultra-pure water were prepared to 15 mM (i.e., well above the *cmc*) and filtered for dynamic light scattering (DLS) studies. Figure 4 shows that these surfactants, at 15 mM, form particles ranging from 0.7–1.1 nm in diameter, typical for diameters for spherical micelles [12, 13]. What is noteworthy is the size order for *n*: 2 (1.15 nm) > 4 (0.86 nm) > 3 (0.74 nm); that is, the smallest micelles are formed from the surfactant with 3 carbons in

Table 1 Comparison of cmc values from this and other studies

Surfactant	Cmc/mM					
	RDS	SB	[24]	[16]	[17]	[18]
12-2-12	0.87±0.03	–	–	–	0.94	0.89±0.04
12-3-12	0.95±0.04	0.98	0.96±0.03	0.94	1.02	0.98±0.04
12-4-12	1.03±0.04	1.23	1.17±0.4	1.17	1.40	1.17±0.04

Table 2 Comparison of α , ΔG_{mic} and ΔG_{cal} determined by this and other studies

Surfactant	α				ΔG_{mic}^1 kJ mol ⁻¹			ΔG_{cal}^2 kJ mol ⁻¹
	RDS	SB	[17]	[18]	RDS	SB	[24]	
12-2-12	0.14 ± 0.02		0.16	0.18 ± 0.02	24.6	–	–	–30.4
12-3-12	0.20 ± 0.02	0.19	0.21	0.23 ± 0.02	23.2	23.3	30.1	–29.9
12-4-12	0.24 ± 0.03	0.28	0.26	0.26 ± 0.02	22.3	21.8	29.2	–30.9

¹Values reported for RDS and SB used Eq. (1) and values reported in ref 24 used: $\Delta G_{\text{mic}} = (1 + \beta)RT \ln(\text{cmc})$

²Determined by NanoAnalyze™

the linker (Table 2). However, the measured hydrodynamic diameters assume spherical micelles. Micelle size and shape for both single and double chained amphiphiles were considered by Tanford in 1972 [21]. His findings showed that such molecules can form a variety of structures from bilayers to cylindrical micelles to vesicles and globular micelles. In addition, the aggregation number for globular micelles depends upon the shape of the assembled structures, whether spherical or ellipsoid [21]. Indeed, the reported literature has provided DLS data to support these potential structures [9–12]. Thus, the differences observed in micelle size here are most likely due to difference in micelle shape. This is also in agreement with the data set of Romsted and coworkers that notes 12-2-12 surfactant begin to grow at approximately 4.0 mM and 12-3-12 and 12-4-12 surfactants yield spherical micelles [17].

It is important to note that these determinations were carried out at 15 mM surfactant—the same concentration used in the ITC studies. Hence, the ITC studies will provide the enthalpy of demicellization of these micelles.

Assuming the micelles are spherical, the surface area of the micelle (Table 2) is simply

$$A = 4\pi r^2 \quad (2)$$

The critical packing parameter, P , is determined by [13, 22]

$$P = V_{\text{hydrophobic}} / (a_0 \times l_0) \quad (3)$$

where $V_{\text{hydrophobic}}$ is the hydrophobic volume of the hydrophobic chain determined using:

$$V_{\text{hydrophobic}} = 2V \quad (4)$$

where V is the volume of the alkyl chain and each surfactant has 2 such chains.

$$V = (27.4 + 26.9m) \times 10^{-3} \text{ nm}^3 \quad (5)$$

Finally, a_0 is the average parking area of a single surfactant and l_0 is the length of the hydrophobic chain [13, 17]

$$l_0 = (0.15 + 0.1265m) \text{ nm} \quad (6)$$

For $m = 12$ (number of carbons in the long chain), $V_{\text{hydrophobic}} = 0.70 \text{ nm}^3$ and $l_0 = 1.67 \text{ nm}$.

Using the values for a_0 reported by Alami [16] for the 12-3-12 and 12-4-12 and extrapolation to $n = 2$ for the 12-2-12 surfactant yielded the values of P in Table 3. For values of $P \leq 1/2$, the surfactants form small micelles. For values of P between $1/2$ and 1, surfactants form bilayers or vesicles [13]. Hence, the larger values of both D_h and P for the 12-2-12 surfactant suggest a different self-assembled structure for this surfactant versus the surfactants with longer more flexible linkers.

ITC determinations

Experimentally, we found it easier to titrate the surfactant at concentrations greater than the cmc into water than to titrate water into micelles. Thus, aqueous solutions of each surfactant were titrated into pure water to determine the enthalpy of demicellization.

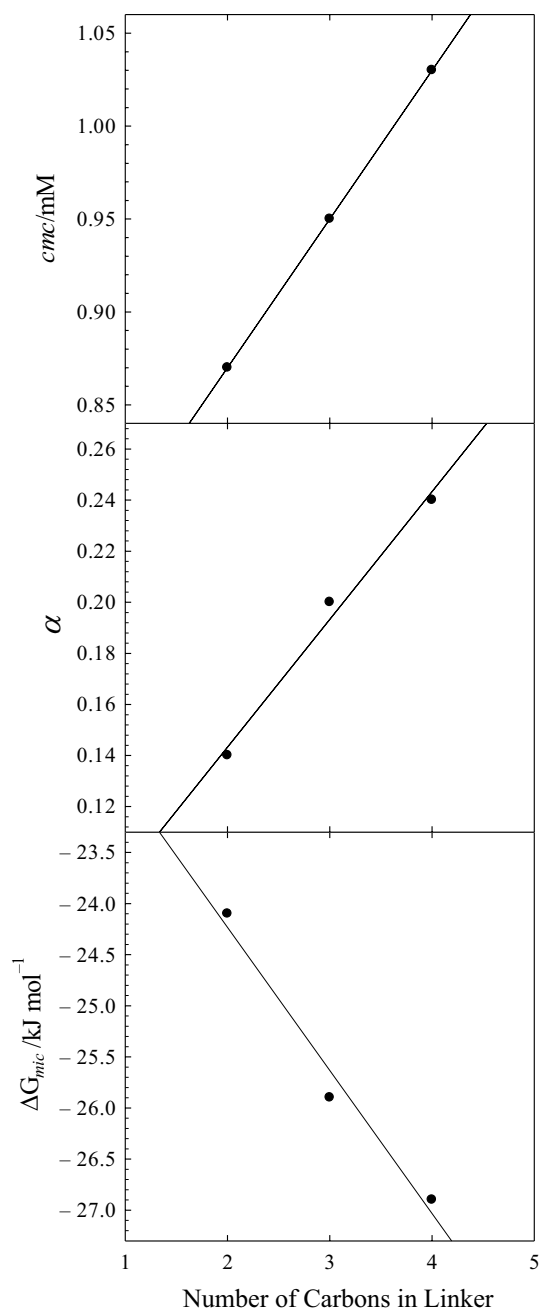


Fig. 3 Dependence of cmc , β and ΔG_{mic} on linker number

Demicellization is enthalpically unfavorable and entropically driven

The left panel of Fig. 5 shows the isotherms for the titration of the 12-2-12 surfactant into water as a function of temperature. As expected, demicellization is endothermic. Similar isotherms were obtained with the 12-3-12 and 12-4-12 surfactants. In these experiments, 2 L of surfactant at 15 mM

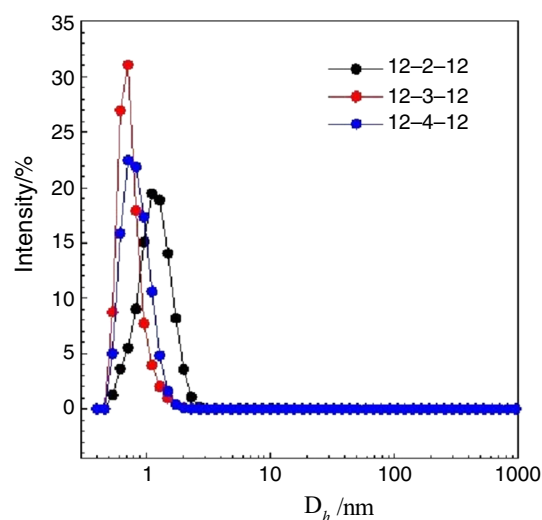


Fig. 4 Intensity-weighted particle distributions for the 12- n -12 surfactants at 25 °C

Table 3 Size parameters for micelles

n	Diameter of micelle/nm	Surface area of micelle/nm ²	Parking area of head group ^[16] /nm ²	P
2	1.15	4.15	0.836	0.50
3	0.736	1.70	1.05	0.39
4	0.864	2.34	1.16	0.36

was titrated into 300 L of water. Early in the titration, the concentration of surfactant in the cell will be much less than the cmc and hence complete demicellization will

occur with each injection. However, as the titration continues, the concentration of surfactant in the cell approaches the cmc and demicellization will diminish until, later in the titration, only dilution of micelles is occurring with subsequent injections. The software of the ITC (NanoAnalyzeTM) determined the enthalpy (ΔH_{cal}), the entropy (ΔS_{cal}) and free energy (ΔG_{cal}) of demicellization. The resultant thermodynamic parameters for the titration of the 12- n -12 surfactants into water at 25 °C are graphically represented in the right panel of Fig. 5. As can be seen, the demicellization is energetically favored and entropically driven. Furthermore, the magnitude of the enthalpy and entropy changes of the 12-2-12 surfactant are larger than the values of the 12-3-12 and 12-4-12 surfactants which is consistent with the observation that later two surfactants are spherical micelles and the 12-2-12 surfactant should be a prolate aggregate undergoing demicellization at these concentrations.

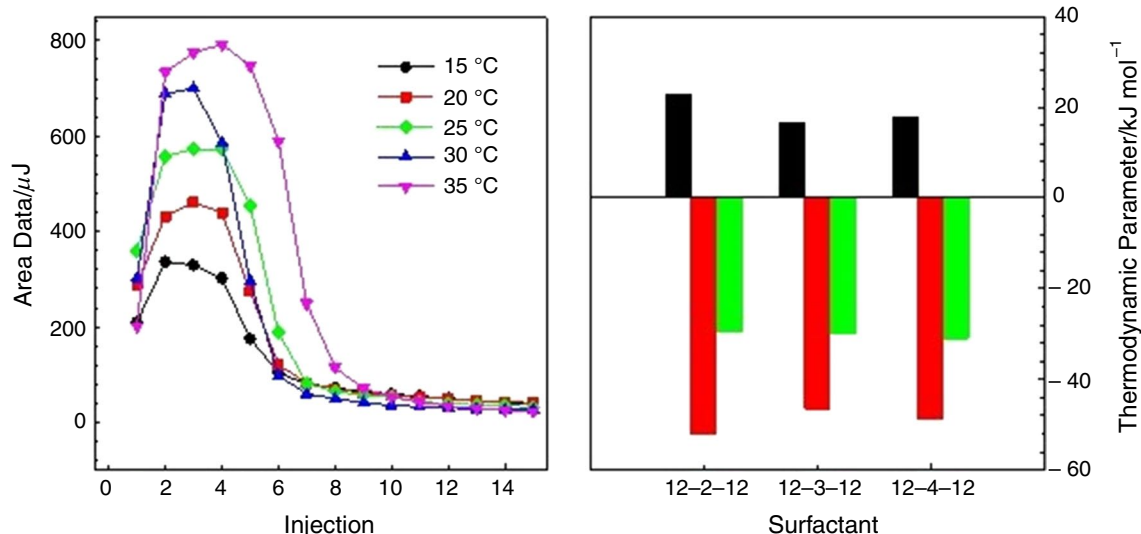


Fig. 5 Left panel: the isotherms for the titration of the 12-2-12 surfactant into water at 15 °C (black squares); 20 °C (red circles); 25 °C (green diamonds); 30 °C (blue up triangles) and 35 °C (violet down

triangle). Right panel: ITC determined ΔH_{cal} (black); $-T\Delta S_{\text{cal}}$ (red); and ΔG_{cal} (green) for the titration of the 12-*n*-12 micelle into water at 25 °C. (Colour figure online)

The thermodynamics of demicellization are dependent upon both *n* and *T*

While ΔH_{cal} values range from 16.6 kJ mol^{-1} to 22.6 kJ mol^{-1} (i.e., $\Delta\Delta H_{\text{cal}} = 6.0 \text{ kJ mol}^{-1}$) and $T\Delta S_{\text{cal}}$ values range from -46.5 to $-52.0 \text{ kJ mol}^{-1}$ (i.e., $\Delta(T\Delta S_{\text{cal}}) = 5.5 \text{ kJ}$

mol^{-1}) at 25 °C, free energy values, ΔG_{cal} , have a much smaller range of values from -30 to $-29.4 \text{ kJ mol}^{-1}$ (i.e., $\Delta\Delta G_{\text{cal}} = 1.5 \text{ kJ mol}^{-1}$). Hence, differences in enthalpies are compensated by differences in entropies leading to small differences in free energies.

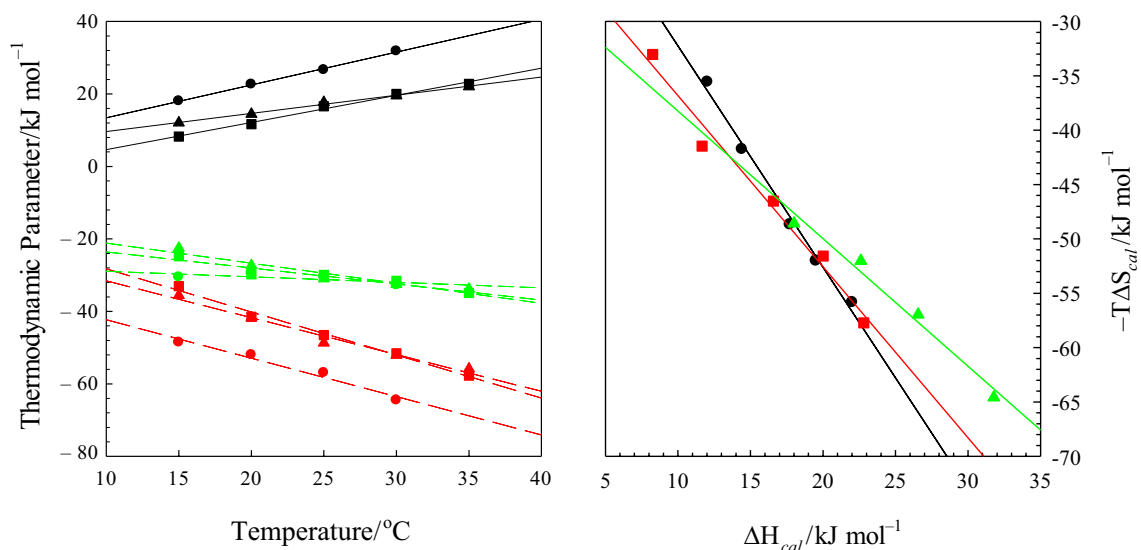


Fig. 6 Left panel: the temperature dependence of ΔH_{cal} (black), $-T\Delta S_{\text{cal}}$ (red) and ΔG_{cal} (green) for the 12-2-12 (squares), 12-3-12 (circles) and 12-4-12 (triangles) surfactants with regression lines (solid black, ΔH_{cal} ; medium dash red, ΔS_{cal} ; short dash green, ΔG_{cal}).

Right panel: the enthalpy–entropy compensation for the 12-2-12 (black circles), 12-3-12 (red squares) and 12-4-12 (green diamonds) with corresponding regression lines. (Colour figure online)

Titrations were repeated at temperatures ranging from 15 to 35 °C. The effect of temperature on the measured thermodynamic values is shown in Fig. 6 (left panel). Whereas enthalpy increases with temperature, both entropy and free energy decrease with increasing temperature. Hence, demicellization is: (1) enthalpically unfavorable and becomes even more unfavorable with increasing temperature; and (2) entropically favorable and becomes even more favorable with increasing temperature. As a result, the enthalpy–entropy compensation shown in Fig. 6 (Right Panel) gives rise to a favorable free energy with little temperature dependence.

Isothermal titration calorimetry has been used to examine the influence of linker length on the thermodynamics of micellization for Gemini surfactants [23–26]. For example, Bendjeriou et al. [25] examined the micellization of Gemini surfactants with dimethyldodecanyl ammonium groups separated by a hydrophilic linker $-\text{CH}_2(\text{CH}_2\text{OCH}_2)_x$, where $x = 2, 3, 6$ and 7 . For these surfactants, micellization was found to be enthalpically favorable. The free energy of micellization, ΔG_{mic} as determined from conductivity studies became less favorable as the linker length (x) increased. Similarly, Lu et al. [23] examined Gemini surfactant with diethyldodecyl ammonium groups separated by a hydrophobic linker $-(\text{CH}_2)_y$, where $y = 4, 6, 8, 10$ and 12 . Micellization was also enthalpically favorable for these surfactants, and ΔG_{mic} determined from conductivity studies also becomes less favorable with increasing linker length.

Literature values of ΔH_{mic} for these 12- n -12 surfactants are scarce. Table 4 compares our determined values ($\Delta H_{\text{mic}} = -\Delta H_{\text{cal}}$) to literature values at different temperatures. We also carried out the ITC experiments at 15 and 20 °C but no literature values could be found for these temperatures. As can be seen, our calorimetrically determined ΔH_{mic} values compare quite well to literature values for the 12-2-12 surfactant at 25 and 35 °C as well as for the 12-3-12 at 30 °C and 35 °C. The values for ΔC_p do not agree very well although our values were determined at 5 temperatures.

Table 2 shows the values for ΔG_{mic} determined by us for the 12-2-12, 12-3-12 and 12-4-12 surfactants, and the

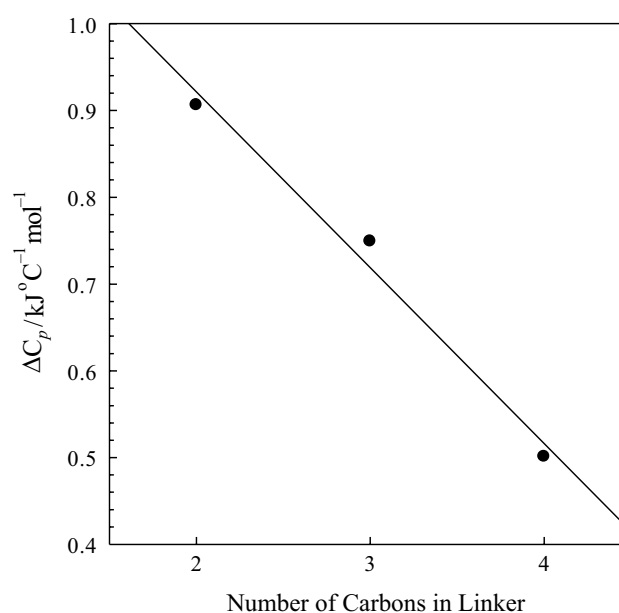


Fig. 7 Dependence of ΔC_p on linker number

value determined by Bai et al. [24] for the 12-3-12 and 12-4-12 surfactant. Also included in Table 2 are the ΔG_{cal} values determined by our ITC studies. As can be seen, there is reasonable good agreement between the ΔG_{mic} values determined in the RDS and SB laboratories with the ΔG_{cal} determined values slightly higher but in general agreement with Bai et al. [24].

ΔC_p is linearly dependent on n

The slopes of the least squares linear fits for the plot in Fig. 6, shown in Table 1, reveal the temperature dependence of each thermodynamic parameter. In the case of enthalpy, the slopes of the lines reveal the difference in heat capacity (ΔC_p) between the micelle and single molecule:

$$\Delta C_p = C_{p,\text{single molecule}} - C_{p,\text{micelle}} \quad (7)$$

Figure 7 shows that ΔC_p decreases in a linear fashion with increasing number of carbons in the linker. The ΔC_p

Table 4 Comparison of ΔH_{mic} and ΔC_p values from literature values to those determined in these studies (in parenthesis)

Surfactant	$\Delta H_{\text{mic}}/\text{kJ mol}^{-1}$			$\Delta C_p/\text{kJ K}^{-1} \text{mol}^{-1}$
	25 °C	30 °C	35 °C	
12-2-12	– (–17.7 ± 0.43)	– (19.5 ± 0.57)	–21[27] (–22.2 ± 0.75)	– (–0.91 ± 0.09)
12-3-12	–5.70 ± 0.11[24] (–16.5 ± 0.44)	15.69 ± 0.47[24] (–20.0 ± 0.54)	–24.85 ± 0.75[24] (–22.0 ± 0.34)	–1.92 ± 0.15[24] (–0.76 ± 0.11)
12-4-12	–4.15 ± 0.10[24] (–26.6 ± 0.62)	–9.38 ± 0.28[24] (–31.8 ± 0.75)	–14.55 ± 0.44[24] –	–1.04 ± 0.08[24] (–0.50 ± 0.04)

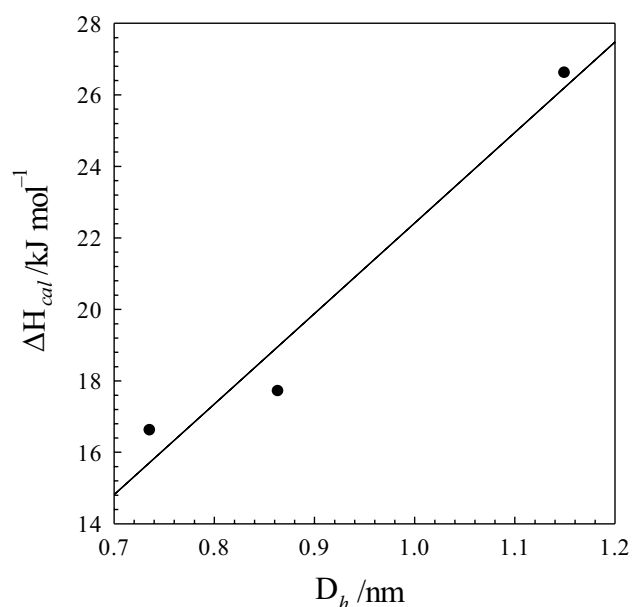


Fig. 8 Dependence of enthalpy of demicellization (ΔH_{cal}) and hydrodynamic radius (D_h) of formed micelle

values reported here, ranging from 500 to 900 J mol⁻¹ °C⁻¹, are similar to those reported by Bijma [23] for single chained surfactants with ΔC_p values ranging from 375 to 600 J mol⁻¹ K⁻¹ but lower than those reported by Bai et al. for the 12-3-12 and 12-4-12 surfactants [24]. Since demicellization should lead to a large change in the water-accessible nonpolar surface area (ΔA_{np}), large ΔC_p s would be expected [28].

Conclusions

We have investigated the physical properties of simple Gemini surfactants with linkers of 2 to 4 carbons. All three surfactants form micelles at concentrations near 1 mM and which have hydrodynamic diameters of 0.73 to 1.2 nm. Further, there are good linear correlations between number of carbons in the linker and certain physical properties such as cmc, α and ΔG_{mic} as determined by conductivity studies, and between number of carbons in the linker and ΔC_p as determined by ITC.

The cmc values obtained by conductivity are similar to those reported in the literature [9, 16, 17, 24]. In addition, the free energies of micelle formation obtained via ITC determinations are similar in sign and magnitude to those obtained from conductivity studies. It is interesting to note that the 12-2-12 surfactant has a significantly higher ΔH than the other surfactants with more flexible linkers. The 12-2-12 also forms the largest micelles of the

three surfactants which would incorporate more surfactant molecules into the micelle; thus, a larger enthalpy change for demicellization. As shown in Fig. 8, there appears to be good correlation between the enthalpy of demicellization and the hydrodynamic radius of the formed micelle.

We are currently carrying out ITC and DLS studies of the 12-5-12 and 12-6-12 surfactants to expand the database.

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Author contributions Tom Sutorius was involved in data acquisition (ITC, DLS), analysis and manuscript preparation. Mikeal McKim took part in data acquisition (DLS), analysis and manuscript preparation. Derek Aquilar contributed to data acquisition (ITC, DLS, conductivity), analysis and manuscript preparation. Hellen Nembaware prepared data acquisition (DLS) and analysis. Steven Bachofer was provider of surfactants and took part in data acquisition (conductivity), analysis, manuscript preparation and editing. Richard D. Sheardy was involved in data acquisition (ITC, DLS, conductivity), analysis, manuscript preparation and project management.

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