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m-s-m cationic gemini and zwitterionic surfactants – a thermodynamic analysis of their mixed micelle formation

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Micelle formation enthalpies ($\Delta_{mic}H$ values) have been calorimetrically determined at 298 K for three sets of mixed zwitterionic/cationic gemini systems consisting of *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (ZW3-12) and a series of structurally related gemini surfactants, the *N,N'*-bis(dimethyldodecyl)-α,ω-alkanediammonium dibromide (12-*s*-12) systems. From the experimental and the estimated ideal micelle formation enthalpies, the excess enthalpies were obtained. The degrees of nonideality of the interaction in the mixed micelle (β^m) from our previous work was used along with the excess enthalpy values to determine excess thermodynamic quantities of the surfactants in the mixed system according to Regular Solution Theory (RST) and Motomura's theory. The excess enthalpies for the ZW3-12/12-4-12 were positive in magnitude and rose sharply when small amounts of the zwittergent were distributed into the gemini micelles. The excess enthalpies for the ZW3-12/12-5-12 and the ZW3-12/12-6-12 systems were also >0 kJ mol^{-1}, and as a function of zwittergent composition, were quite different to those of the ZW3-12/12-4-12 mixed micelles. These results indicate that the heat of mixed micelle formation is strongly dependent on electrostatic interactions and the structure of the surfactants involved, specifically, the length of the tether group for the 12-*s*-12 gemini surfactants. From the calorimetric data and the application of RST and Motomura's theory, we have obtained estimates of the excess Gibbs energy and entropy of mixing. An analysis of the three thermodynamic properties suggests that the relative contributions of enthalpic and entropic effects to nonideal behavior for mixed micelles involving gemini surfactants are strongly dependent on the gemini structure.

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Introduction

Surfactants possessing unusual architectures have been gaining increasing attention in the literature over the last decade. One such example of these architectures are so-called gemini or dimeric surfactants;[1–8] they have a structure that can be represented as two monomeric surfactant units connected at or near the head groups by a spacer. This kind of architecture provides solution properties that are dependent upon the nature and size of the head groups as well as the spacer groups. Gemini surfactants are found to be superior to corresponding conventional monomeric surfactants in a number of ways, including lower critical micelle concentration (cmc) values, better lime-soap dispersion, and better wetting properties.[8–12]

Gemini surfactants, like most conventional surfactants, are likely to be used in mixtures in applications. Zwitterionic surfactants are similar to gemini surfactants in that they have a dipolar head bearing both positive and negative charges, but generally only a single tail.[13–22] In general, zwitterionic surfactants are mild to skin and eyes, have low toxicity, and display excellent water solubility, high foam stability, and excellent surface tension reducing properties.[19,23,24] In combination with other surfactants, zwitterionic surfactants find applications in laundry detergents, shampoos, and other cosmetic products.

Although it is well known that surfactant mixtures often have improvements in performance of their mixtures *versus* the individual surfactant (*i.e.*, synergism),[25–34] there are few studies in the literature that examine the intricate molecular details that govern the thermodynamics of the formation of mixed micelles. In fact, most of the studies of synergism in mixed surfactant systems in the literature have dealt with how the critical micelle concentration (cmc value) compares in the mixture *versus* an ideal cmc calculated using an equation like that of Clint.[35] While the mixture cmc is important, developing a more detailed fundamental understanding of the behavior of the surfactants in the formation of the mixed micellar solutions

is required for enhancing their performance in applications where improved wettability and detergency is required.

Synergism is often modeled in the literature by employing the regular solution theory (RST)[36] with an interaction parameter β^m. Although RST has proven quite successful in accounting for the nonideal behavior of a number of binary surfactant systems, it does not adequately address the excess Gibbs energy in mixed surfactant systems.[37] In the context of RST, the interaction parameter, β^m, quantifies the nonidealities between the surfactants in the real mixed micelles relative to the interactions in the ideal mixed micelles of the pure surfactant micelles as being wholly enthalpic. Other thermodynamic treatments have been developed to interpret the deviations from the ideal micellar composition in terms of both enthalpic and entropic contributions.[38] Motomura's theory is one such theory,[39–43] and it is often used in the literature for the calculation of the Gibbs energy of micelle formation as a measure of molecular interactions.

Although there have been numerous reports on synergism in mixtures involving gemini surfactants with ionic and non-ionic conventional surfactants,[31,44–57] there are only a few reports in the literature where a detailed thermodynamic analysis of synergistically interacting surfactant systems have been carried out calorimetrically.[46,49,58–60] In this paper, the thermodynamics of the mixed micellization process for three sets of mixed zwitterionic/cationic gemini systems have been obtained using titration calorimetry (ITC). Specifically, the mixed surfactant systems investigated here consist of three members of the N,N'-bis (dimethyldodecyl)-α,ω-alkanediammonium dibromide (12-s-12) series (m-s-m gemini surfactants 12-4-12, 12-5-12, and 12-6-12) and the zwitterionic surfactant N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (ZW3-12). The interaction parameters from our previous paper have been used with the calorimetrically determined enthalpies to obtain the excess enthalpies and Gibbs energies on the basis of regular solution theory. Motomura's theory was also used to obtain excess thermodynamic functions, namely the excess Gibbs energy and entropy. The activity coefficients of each surfactant in the mixed micelles are obtained, and the tendency of surfactants to form mixed micelles and the interactions between the constituent surfactants are discussed.

Experimental

Materials

N,N-Dimethyldodecylamine, 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane having purities of 97%, 99%, 97%, and 97% respectively were received from Sigma-Aldrich. N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (ZW3-12) with purity of 99% was received from Sigma-Aldrich and used without further purification.

Methods

**Gemini surfactant synthesis.** The N,N'-bis(dimethyldodecyl)-α,ω-alkanediammonium dibromide (12-s-12) surfactants were prepared, according to the method described by Wettig and Verrall[61,62] and in our previous paper.[31]

Calorimetric titration experiments. Microcalorimetric titration measurements were carried out using an isothermal calorimeter (model number CSC 4200, ±0.01 µW accuracy, from Calorimetry Sciences Corporation) having a 1300 µL titration cell and a 250 µL syringe, with continuous/constant stirring at 25 °C. A concentrated solution containing the zwittergent and the appropriate gemini was titrated into triply deionized water (18 MΩ cm^{-1}); generally a minimum of 16 injections were used in each experiment. The heat generated by the thermal event was monitored as the gemini/zwittergent mixture was titrated into water above and below the cmc of the mixed micellar system. The instrument was calibrated repeatedly over the course of the experiments. Titrations were performed in duplicate or triplicate; the deviations reported in the measured enthalpy values represent the maximum deviation from the average of the three runs. As these maximum deviations changed little for the various solutions investigated, the range quoted for the triplicate runs was taken to represent the maximum deviation observed in the experiments. The raw data obtained from the instrument for all experiments was processed using the BindWorks 3.1 software provided with the calorimeter.

Results and discussion

Cmc values and mixed micelle thermodynamics

For the zwittergent/gemini surfactant mixed micelle, the $\Delta_{mic}H$ values refer to the enthalpy change that occurs when N_S moles of surfactant S (charge a), N_C moles of counterion C (charge b), and N_Z moles of zwittergent Z aggregate in aqueous solution to form the mixed micelle, M, of charge $\pm v$

$$N_sS^a + N_cC^b + N_zZ \rightleftharpoons M^{\pm v} \tag{1}$$
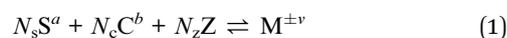
A typical plot of the heat evolution from the surfactant demicellization process being monitored is presented in Fig. 1a for the dilution of a 50.12 mM solution of ZW3-12, and Fig. 1b for the dilution of an approximately 50 mM solution containing both the zwittergent and the 12-4-12 gemini surfactant at a total fraction of zwittergent (α_{ZW3-12}) equal to 0.30. The regions in Fig. 1a correspond to (i) the dilution of the concentrated micellar containing solution to a more dilute micellar containing solution; (ii) the dilution of the concentrated micellar containing solution to a dilute solution containing surfactant monomers; and (iii) the transition between a solution containing predominantly monomers and a micellar containing solution. In order to evaluate the calorimetric cmc values, we have used the method of Yan,[63,64] and van Os.[65] The $\Delta_{mic}H$ values are obtained directly from the difference between the observed enthalpies in the two linear regions of the enthalpic titration curve; the cmc values are taken as the concentration where the deviation in linearity first appears in the transition region labelled (iii) in Fig. 1. The enthalpy change in that region is equal to the enthalpy change that occurs when the monomers transition to stable micelles. The enthalpy data for the three 12-
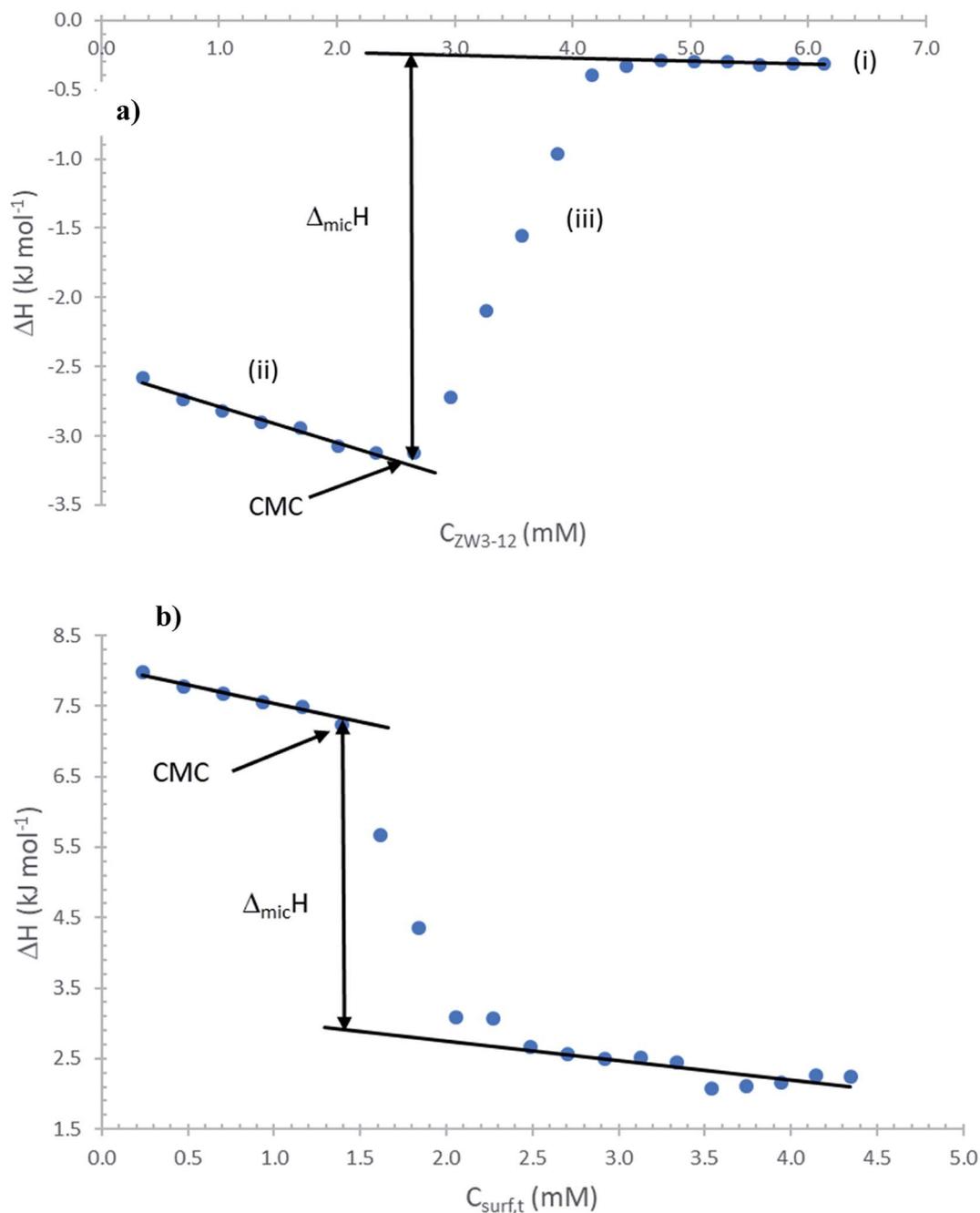
Fig. 1 Enthalpograms for the titration of (a) 50.12 mM ZW3-12; (b) titration of a 47.58 mM ZW3-12/12-4-12 at $\alpha_{ZW3-12} = 0.30$ into water at 298.2 K.

s-12 surfactants and the mixed ZW3-12/12-s-12 systems are presented in Fig. 2 and given in Table 1 as a function of the composition of the surfactant solution (α_{ZW3-12}). In all cases, break points in the enthalpic titration curves correspond to the calorimetric cmc values and are in good agreement with the conductometric cmc values from our previous work.[31] Fig. 2 clearly demonstrates that the enthalpy of micelle formation changes quite substantially as the composition of the mixed surfactant system is varied. As well, the cmc values from the previous conductometric investigations exhibit identical trends as the cmc values obtained calorimetrically. It could be argued

that the deviations from ideal behavior seem to be more pronounced using the calorimetric cmc values *versus* the conductometric cmc values of the previous paper. This may indicate that the calorimetric technique is more sensitive to deviations from ideality *versus* the conductometric cmc values; this is currently being investigated in the lab for some well-known classical surfactant mixtures.

In order to assess the ideal/nonideal nature of the micelle formation enthalpies, it is necessary to estimate the ideal micelle formation enthalpies by first calculating the ideal micellar mole fractions. Several theories have been developed to
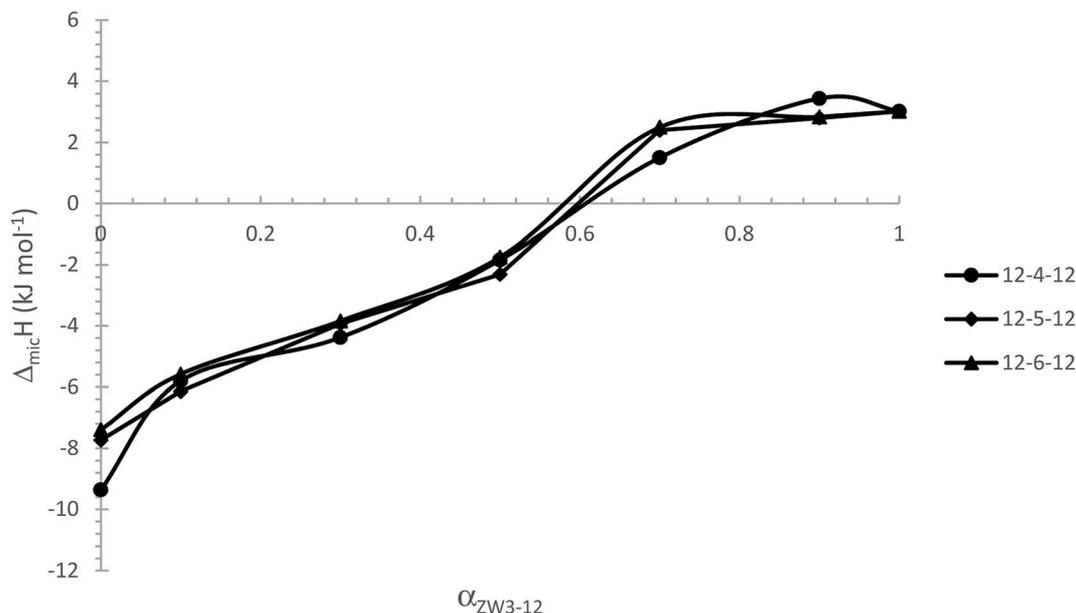
Fig. 2 Calorimetric enthalpies of mixed micelle formation for the ZW3-12/12-5-12 system as a function of the mole fraction of zwitterionic surfactant in the surfactant mixture (α_{ZW3-12}): ● 12-4-12; ◆ 12-5-12; ■ 12-6-12.

predict and analyze ideal cmc values, and hence, the ideal mole fractions of surfactant in the micellar phases in binary surfactant mixtures. Clint's eqn (2) is one such treatment.

$$1/\text{CMC}_{\text{mix}} = \sum_i \alpha_i / \text{CMC}_i \qquad (2)$$

In this equation CMC_{mix} is the cmc of the mixture; α_i is the mole fraction of each component i in the solution; and CMC_i is the cmc of each component i.[35,66] Therefore, for a zwittergent/gemini surfactant mixture:

Table 1 Mixture micelle formation enthalpies (±0.2 kJ mol^{-1}), mixed cmc values, and estimates for the cmc^{id}, X^{id}_{ZW3-12}, and ideal micelle formation enthalpies based on Clint's equation

α_{ZW3-12}	$\Delta_{mic}H$ (kJ mol^{-1})	Cmc (mM)	Cmc^{id} (mM)	X^{id}_{zw3-12}	$\Delta_{mic}H^{id}$ (kJ mol^{-1})
12-4-12					
0.000	−9.36	1.10	1.10	0.000	−9.36
0.100	−5.80	1.25	1.17	0.044	−8.81
0.300	−4.38	1.37	1.33	0.152	−7.48
0.500	−1.84	1.52	1.55	0.295	−5.71
0.700	1.50	1.58	1.86	0.494	−3.25
0.900	3.44	2.22	2.31	0.790	0.42
1.000	3.02	2.63	2.63	1.000	3.02
12-5-12					
0.000	−7.73	0.998	0.998	0.0000	−7.73
0.100	−6.14	1.07	1.06	0.040	−7.30
0.300	−3.93	1.22	1.23	0.140	−6.23
0.500	−2.31	1.47	1.45	0.275	−4.77
0.700	2.40	1.63	1.76	0.470	−2.68
0.900	2.80	1.98	2.26	0.774	0.59
1.000	3.02	2.63	2.63	1.000	3.02
12-6-12					
0.000	−7.39	0.986	0.986	0.0000	−7.39
0.100	−5.58	0.993	1.05	0.040	−6.97
0.300	−3.84	1.06	1.21	0.138	−5.95
0.500	−1.75	1.15	1.43	0.273	−4.55
0.700	2.50	1.31	1.75	0.467	−2.53
0.900	2.84	1.67	2.25	0.771	0.64
1.000	3.02	2.63	2.63	1.000	3.02

$$1/\mathrm{CMC_{mix}} = \alpha_{\mathrm{ZW3\text{-}12}}/\mathrm{CMC_{ZW3\text{-}12}} + \alpha_{\mathrm{gem}}/\mathrm{CMC_{gem}} \qquad (3)$$

$\mathrm{CMC_{mix}}$, $\mathrm{CMC_{ZW3\text{-}12}}$ and $\mathrm{CMC_{gem}}$ represent the critical micelle concentrations of the mixed surfactant, ZW3-12, and the corresponding gemini surfactant, and α_J represents the mole fraction of each surfactant in the ideal mixed system.[67] Clint's equation works well for binary mixtures of homologous surfactants in which the head groups are similar and/or the differences in the tail architectures are not substantial and will serve as our framework for discussing the interactions that lead to nonideality in these surfactant mixtures.

From the ideal mole fractions, ideal estimates of the micelle formation enthalpies were calculated as follows

$$\Delta_{\mathrm{mic}}H^{\mathrm{id}} = X^{\mathrm{id}}_{\mathrm{ZW3\text{-}12}}\Delta_{\mathrm{mic}}H(\mathrm{ZW3\text{-}12}) + X^{\mathrm{id}}_{\mathrm{gem}}\Delta_{\mathrm{mic}}H(\mathrm{gem}) \qquad (4)$$

where the ideal mole fractions of the surfactants in the micelle are calculated using the ideal cmc values (Clint's equation) and the cmc's of the pure surfactants. In Fig. 3a–c, we compare the ideal enthalpies (obtained from eqn (4)) with the experimental values for the ZW3-12/12-s-12 gemini systems. It can be seen from Fig. 3 that the ideal enthalpies are in reasonable agreement with calorimetric enthalpies over most of the mole fraction range, except in the high $\alpha_{\mathrm{ZW3\text{-}12}}$ range, where it is clear that the mixed micelle enthalpies are considerably more positive than those predicted ideally! We will return to these differences in the discussion of the excess thermodynamic properties below.

The standard Gibbs energy of micellization ($\Delta_{\mathrm{mic}}G$) represents the decrease in the molar Gibbs energy when one mole of surfactant transfer from the aqueous phase to the micellar phase. Using the phase separation model, for a zwitterionic micellar system, it is calculated as follows

$$\Delta_{\mathrm{mic}}G = RT\ln X_{\mathrm{cmc}} \qquad (5)$$

Zana has derived the standard Gibbs energy changes for several different surfactant architectures, including bolaform surfactants and gemini surfactants.[68] For gemini surfactants, the standard Gibbs energy of micellization is given by

$$\Delta_{\mathrm{mic}}G = (0.5 + \beta)RT\ln X_{\mathrm{cmc}} \qquad (6)$$

where β represents the degree of counterion binding and can be estimated from the conductivity data in our previous paper.[31] In this paper, we treat the mixed systems of the gemini and the zwitterionic surfactant as gemini surfactants to which zwittergent has been added. Hence, eqn (6) was used to calculate the micellization enthalpies for all systems where the gemini surfactants are present. The entropy of micellization ($\Delta_{\mathrm{mic}}S$) can be calculated from the Gibbs equation as follows

$$\Delta_{\mathrm{mic}}S = (\Delta_{\mathrm{mic}}H - \Delta_{\mathrm{mic}}G)/T \qquad (7)$$

The values of the $\Delta_{\mathrm{mic}}H$, $\Delta_{\mathrm{mic}}G$, and $\Delta_{\mathrm{mic}}S$ are given in Table 2 for all the systems studied here. The cmc of the gemini surfactants is slightly less than that of the ZW3-12, meaning that the standard Gibbs energy change for the formation of the gemini pseudophases is less than that of the zwitterionic pseudophase. The gemini surfactants are also characterized by negative enthalpies of micelle formation, *versus* the positive $\Delta_{\mathrm{mic}}H$ values we observe for ZW3-12 which is likely due to the large attractive interactions between the hydrocarbon tails when the double tailed surfactants are brought in close proximity in the micellar phase. Although this decrease in the enthalpy is partially offset by hydrophobic effects and electrostatic interactions between the doubly charged surfactant
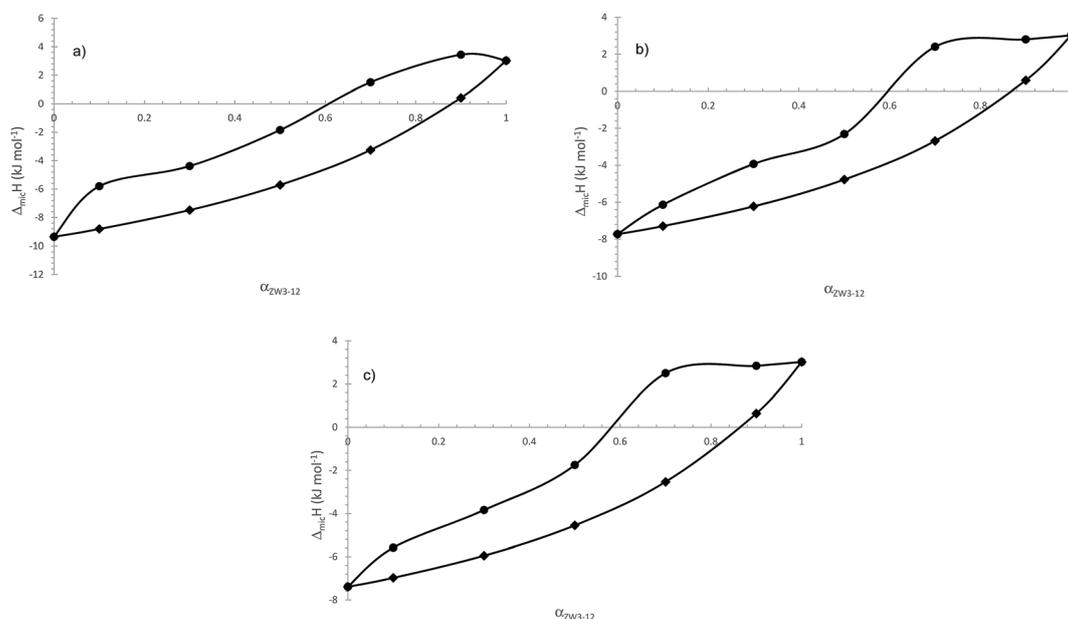

Fig. 3 Experimental (●) and ideal enthalpies (◆) of mixed micelle formation for ZW3-12/12-s-12 systems as a function of the mole fraction of zwitterionic surfactant in the surfactant mixture ($\alpha_{\mathrm{ZW3\text{-}12}}$): (a) 12-4-12; (b) 12-5-12; (c) 12-6-12.

Table 2 Derived thermodynamic data for ZW3-12/12-*s*-12 system as a function of the mole fraction of zwittergent ($\alpha_{ZW3\text{-}12}$)

	12-4-12		12-5-12		12-6-12	
$\alpha_{ZW3\text{-}12}$	$\Delta_{mic}G$ (kJ mol^{-1})	$\Delta_{mic}S$ (J K^{-1} mol^{-1})	$\Delta_{mic}G$ (kJ mol^{-1})	$\Delta_{mic}S$ (J K^{-1} mol^{-1})	$\Delta_{mic}G$ (kJ mol^{-1})	$\Delta_{mic}S$ (J K^{-1} mol^{-1})
0.00	−33.9	82.2	−33.4	86.3	−33.6	88.1
0.10	−33.0	91.1	−32.9	89.6	−32.7	91.0
0.30	−31.5	90.8	−31.7	93.0	−31.8	93.8
0.50	−29.3	92.2	−30.1	93.1	−28.5	89.8
0.70	−27.3	96.7	−26.5	96.8	−26.5	97.2
0.90	−20.6	80.5	−20.4	77.7	−19.7	75.4
1.00	−24.6	92.6	−24.6	92.6	−24.6	92.6

headgroups, the dispersive van der Waal's interactions dominate the total observed enthalpy. In all cases, the $\Delta_{mic}S$ values are positive, reflecting the disruption in the ordering of water molecules surrounding the hydrocarbon chains of the monomeric surfactants in the bulk solution. These positive entropy values are consistent with the decrease in partial molar entropy of the surfactants as they undergo co-micellization being offset by the increase in entropy of the water molecules that are "released" due to aggregation of the surfactants in the micelle interior.

These results indicate that the micellization process for the gemini surfactants investigated here is driven both by entropic (hydrophobic effects) and enthalpic effects (alkyl chain interactions). For ZW3-12, the positive values of both $\Delta_{mic}S$ and $\Delta_{mic}H$ are consistent with the micellization process being entropy driven; this is clearly the case as more zwittergent is present in the mixed micelles, although the increases in enthalpy are greater than that expected of an ideal mixing of the surfactants. We note that, as expected, the enthalpies of mixed

micellization trend towards more positive values as the fraction of zwittergent in the mixed system is increased. However, for low fractions of ZW3-12 in the mixed systems, the increase in the enthalpy is greater than what would be predicted from an ideal mixing of the two micellar pseudophases.

Regular solution theory, as applied to the interaction between two surfactants, uses the micellar interaction parameter, β^m,[69] to discuss the deviations from ideality in the context of micelle formation that can lead to the presence of synergism. While a number of papers in the literature use the existence of a negative β^m parameter to suggest synergistic interactions are taking place between the surfactants comprising the mixed micelles, the following two conditions must be met in order for synergism to exist in mixed micelle formation: (1) β^m must be negative, and (2) $|\beta^m| > |\ln(\text{CMC}_1/\text{CMC}_2)|$.[69]

In Fig. 4, we compare the ideal cmcs (obtained from Clint's equation, eqn (1)) and calorimetric cmcs for the ZW3-12/12-*s*-12 gemini systems. It can be seen from Table 1 that, in agreement with previous conductometric data, the three systems exhibit
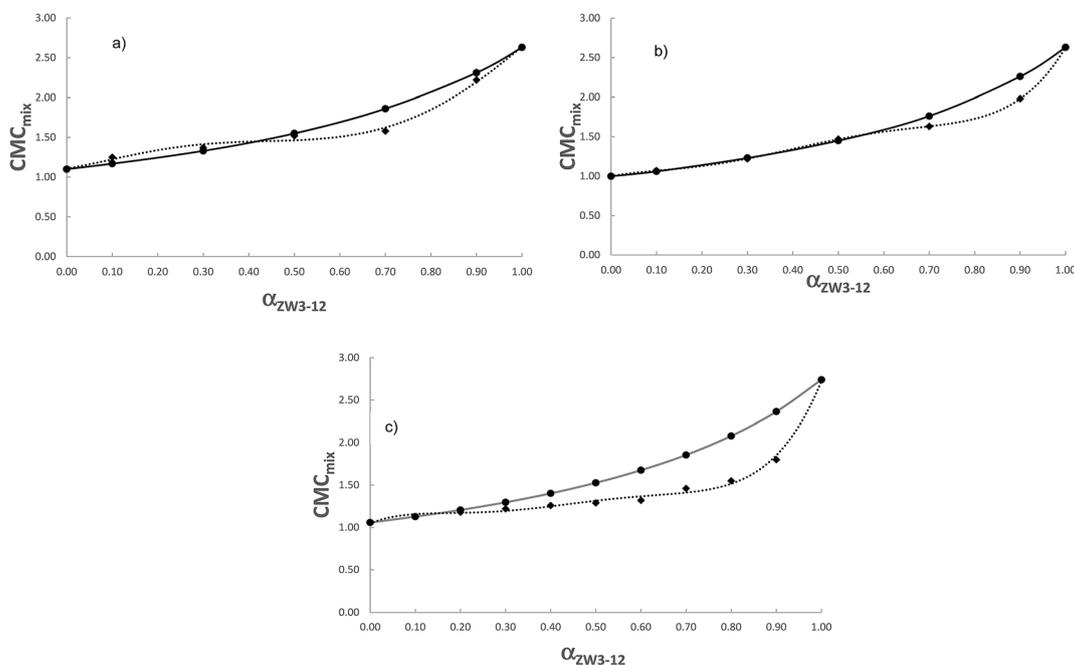

Fig. 4 Comparison between ideal (●) and experimental cmc's (◆) for the ZW3-12/12-*s*-12 system. (a) 12-4-12; (b) 12-5-12; and (c) 12-6-12.

identical trends in the CMC values as a function of the surfactant mixture composition. As was stated in our previous paper, the negative β^{m} values indicate attractive interactions in mixed systems; however, the zwittergent/12-4-12 and 12-5-12 systems only satisfy this condition at $\alpha_{ZW3-12} = 0.9$, whereas the ZW3-12/12-6-12 systems satisfy this above $\alpha_{ZW3-12} = 0.6$. Given the similarities in the trends in the calorimetric cmc values for the ZW3-12/12-s-12 mixed surfactant systems to the conductometric values, we expect a similar conclusion here.

Calculation of excess thermodynamic properties

The excess enthalpies are obtained by subtracting the ideal enthalpies (calculated above) from the calorimetric enthalpies as follows

$$H^{E} = \Delta_{mic}H - \Delta_{mic}H^{id} \tag{8}$$

The excess enthalpies are given in Table 3 and plotted in Fig. 5 as a function of the fraction of ZW3-12 in the total surfactant amount. From Fig. 5, the excess enthalpies are observed to be more endothermic as the zwittergent molecules replace the gemini molecules in the mixed micelle; we also see a very different trend in the H^{E} values for the 12-4-12/ZW3-12 system versus the values for either the 12-5-12/ZW3-12 and 12-6-12/ZW3-12 systems. The H^{E} values for the 12-5-12 and the 12-6-12/ZW3-12 mixed micelles are virtually identical with one another, reflecting a similarity in the way these surfactants interact with each other in the formation of the mixed micelles. This is in excellent agreement with the NMR 2D-NOESY results in our previous paper that indicated differences in the manner in which 12-4-12 self-assembled with the ZW3-12 surfactant versus both the 12-5-12 and the 12-6-12.[31] This can be explained in terms of the change in the radius of curvature of the micelles introduced when the zwittergent surfactants replace the gemini surfactants in the micelle,[70] resulting in a highly asymmetric shape for the excess enthalpy curves for all the ZW3-12/12-s-12 systems with respect to α_{ZW3-12}. If we interpret the excess functions in terms of RST, we would expect the plot of the excess enthalpies to be symmetric as it would only consider pairwise interactions that lead to deviations from ideal behaviour. Clearly, in the systems studied here, the excess enthalpy curves

are characterized by a rapid change in enthalpy versus composition. For the ZW3-12/12-4-12 system, this rapid change in the enthalpy occurs near $\alpha_{ZW3-12} = 0.20$, whereas for the 12-5-12 and the 12-6-12 systems, the rapid enthalpy change occurs near $\alpha_{ZW3-12} = 0.60$. This must be due to the slight extension that occurs in the tether group of the gemini surfactants with the addition of the methylene groups in the spacer, meaning that for the ZW3-12/12-4-12 systems, the enthalpically favourable interactions are weaker and less cooperative. Note that most of the values for H^{E} are about a few kilojoules per mol, consistent with a random arrangement of molecules in the mixed micelle. By combining the NMR-NOESY data from our previous work[31] with the enthalpic data in this paper, we conclude that steric and electrostatic interactions between headgroups and hydrophobic interactions between the surfactant tether groups and the hydrophobic chains play a significant role in the mixed aggregation process.

Regular solution theory calculates the activity coefficients from the mole fractions of the surfactants in the mixed micelles using the following equations

$$f_{Z} = \exp(\beta^{m}(1 - \chi_{Z})^{2}) \tag{9}$$

and

$$f_{gem} = \exp(\beta^{m}(1 - \chi_{gem})^{2}) \tag{10}$$

where the coefficient of proportionality, β^{m}, represents the interaction parameter from our previous paper, f_{Z} and f_{gem} represent the activity coefficients of the zwittergent and gemini surfactants in the micelles, and χ_{Z} and χ_{gem} represent the mole fractions of the zwittergent and gemini in the micellar phases, respectively. The interaction parameter quantifies the enthalpic interactions between different surfactants in the real mixed micelles relative to the interactions in the ideal mixed micelles of surfactants comprising the micelles.[37,71] If the value of β^{m} is negative, it can also indicate the presence of stabilization owing to differences in hydration between the real and the ideal mixed micelles. In RST, since the excess entropy is 0, these enthalpic interactions are the sole contributions to the excess Gibbs energy. Hence, the excess Gibbs energy is calculated from the following equation:[72,73]

$$G^{E} = RT\beta^{m}(\chi_{Z} - \chi_{Z}^{2}) \tag{11}$$

The excess Gibbs energy is a measure of the stability of the real mixed micelle relative to the stability of the ideal mixed micelles. The more negative the value of G^{E}, the more stable the real mixed micelles are compared to aggregates created by mixing the pure micelles in the appropriate proportions. According to RST, this means that the formation of real mixed micelles are intrinsically more favoured than the formation of single surfactant micelles because the ideal micelles are aggregates in which no additional interactions exist!

The activity coefficients, and the G^{E} values calculated according to RST are given in Table 3. From Table 3, we observe that the values of f_{Z} and f_{gem} both decrease at a constant α_{ZW3-12} value. According to Rubingh and Holland,

Table 3 Derived activity coefficients and excess Gibbs energies for ZW3-12/12-s-12 system from RST as a function of the mole fraction of zwittergent (α_{ZW3-12})

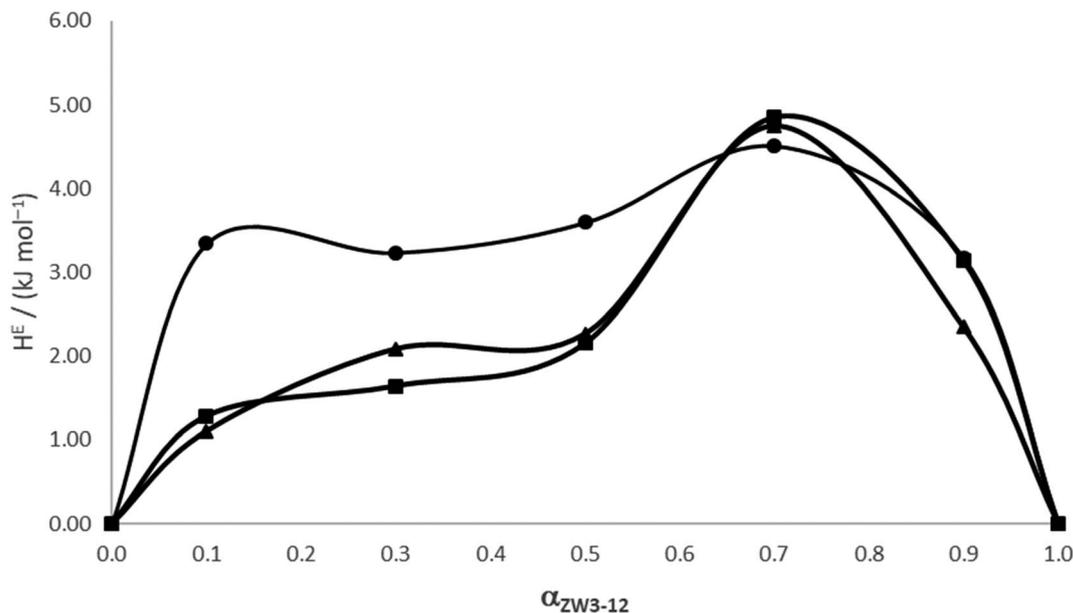| α_{ZW3-12} | 12-4-12 | | | 12-5-12 | | | 12-6-12 | | |
	G^{E} (kJ mol^{-1})	f_{Z}	f_{gem}	G^{E} (kJ mol^{-1})	f_{Z}	f_{gem}	G^{E} (kJ mol^{-1})	f_{Z}	f_{gem}
0.00	0.0	—	1.00	0.0	—	1.00	0.0	—	1.00
0.10	0.0	2.70	0.99	0.0	0.96	0.99	0.0	0.82	1.01
0.30	0.0	1.14	1.00	0.0	0.92	1.00	−0.2	0.73	0.99
0.50	−0.1	0.93	0.99	0.0	0.98	1.00	−0.4	0.70	0.92
0.70	−0.5	0.81	0.83	−0.2	0.90	0.95	−0.6	0.77	0.80
0.90	−0.2	0.94	0.83	−0.3	0.91	0.78	−0.7	0.87	0.53
1.00	0.0	1.00	—	0.0	1.00	—	0.0	1.00	—

Fig. 5 Excess enthalpies of mixing data for ZW3-12/12-s-12 system as a function of the mole fraction of zwittergent (α_{ZW3-12}). ● 12-4-12; ▲ 12-5-12; ■ 12-6-12.

the activity coefficients reflect the strength of the intermolecular interactions that lead to the formation of mixed micelles. The values of the excess Gibbs energies are all quite small, consistent with the values of the interaction parameters from our previous paper. The positive values of G^E for the 12-4-12/ZW3-12 mixed system at low values of α_{ZW3-12} indicate that the Gibbs energy of micelle formation of mixed micelles is more positive than that of ideally mixing micelles, consistent with the interaction between the zwittergent and the gemini leading to micellar destabilization at low values of α_{ZW3-12}, in agreement with the H^E values above.

The deviations from ideal mixing in the micelles can also be categorized by applying the following equations, resulting from Motomura's theory[39–43]

$$G^{M,E} = RT \sum_{i=1}^{2} X_J^M \ln f_J^M \tag{12}$$

Here f_Z^M and X_J^M represent the activity coefficients and mole fractions of the zwittergent (f_Z^M, X_Z^M) and gemini (f_{gem}^M, X_{gem}^M), respectively, in the micelle. These can be calculated by applying the following equations

$$Cmc_{mix}X_Z = C_Z^0 f_Z^M X_Z^M \tag{13}$$

$$Cmc_{mix}X_{gem} = C_2^0 f_2^M X_2^M \tag{14}$$

In this equation Cmc_{mix} is the cmc of the mixture, C_Z^0 and C_g^0 are the cmcs of the pure zwittergent and gemini surfactant, respectively. For a binary mixed surfactant system, X_J^M is obtained using the following equation

$$X_J^M = X_J - \left(\frac{X_J(1-X_J)}{cmc_{mix}}\right)\left(\frac{\partial cmc_{mix}}{\partial X_J}\right) \tag{15}$$

The values of X_Z^M and X_g^M, the activity coefficients, and the $G^{M,E}$ values calculated for all the zwittergent/gemini systems are given in Table 4; the $G^{M,E}$ values are plotted in Fig. 6. The excess entropy is calculated as follows

Table 4 Derived activity coefficients and excess Gibbs energies for ZW3-12/12-s-12 system from Motomura's theory as a function of the mole fraction of zwittergent (α_{ZW3-12})

| α_{ZW3-12}	X_Z^M	X_g^M	f_Z^M	f_g^M	$G^{M,E}$ (kJ mol^{-1})	$S^{M,E}$ (J K^{-1} mol^{-1})
12-4-12						
0.00	0.000	1.000	—	1.00	0.00	0.0
0.10	0.045	0.955	0.49	1.08	0.11	10.9
0.30	0.155	0.845	0.55	1.22	0.19	10.2
0.50	0.301	0.699	0.60	1.35	0.13	11.6
0.70	0.502	0.498	0.68	1.54	0.06	14.9
0.90	0.795	0.205	0.81	1.83	−0.10	11.0
1.00	1.000	0.000	1.00	—	0.00	0.0
12-5-12						
0.00	0.000	1.000	—	1.00	0.00	0.00
0.10	0.042	0.955	0.44	0.98	−0.13	4.1
0.30	0.146	0.854	0.50	1.11	−0.03	7.1
0.50	0.288	0.712	0.58	1.31	0.09	7.3
0.70	0.490	0.510	0.64	1.48	−0.04	16.1
0.90	0.790	0.210	0.76	1.79	−0.23	8.7
1.00	1.000	0.000	1.00	—	0.00	0.0
12-6-12						
0.00	0.000	1.000	—	1.00	0.00	0.0
0.10	0.040	0.960	0.42	0.94	−0.23	4.3
0.30	0.141	0.859	0.45	1.02	−0.25	5.5
0.50	0.280	0.720	0.47	1.08	−0.39	7.2
0.70	0.480	0.520	0.53	1.23	−0.50	16.3
0.90	0.784	0.216	0.65	1.55	−0.60	10.5
1.00	1.000	0.000	1.00	—	0.00	0.0
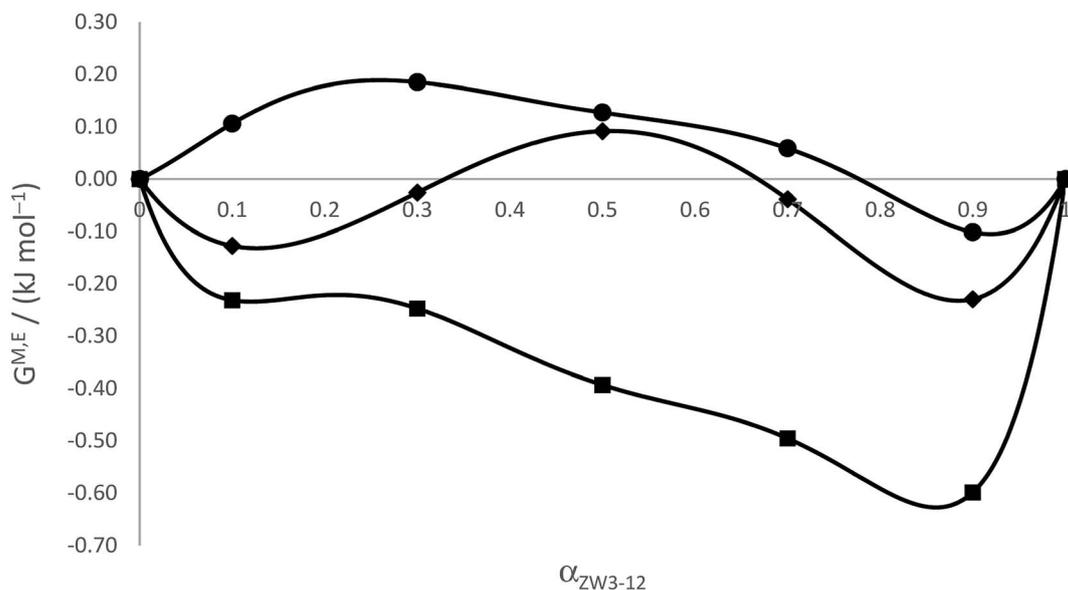
Fig. 6 Excess Gibbs energies of mixing from Motomura's theory for ZW3-12/12-*s*-12 system as a function of the mole fraction of zwittergent (α_{ZW3-12}). ● 12-4-12; ◆ 12-5-12; ■ 12-6-12.

$$S^{M,E} = (H^E - G^{M,E})/T \tag{16}$$

The values for the excess entropy are also presented in Table 4 and plotted in Fig. 7. For the ZW3-12/12-4-12 system, the calculated values of the excess Gibbs energy are small and positive, particularly in the region of low values of α_{ZW3-12}, indicating that mixed micelle formation by these two surfactants is not energetically favoured in this region, in agreement with RST and the excess enthalpies above. This is

likely due to the combination of an increased steric effect due to the size of the zwitterionic headgroup in the ZW3-12, coupled with the presence of the permanent positive charge in the zwitterionic headgroups that leads to significant repulsions as the two dissimilar headgroups attempt to pack in the micellar pseudophase, particularly at low values of α_{ZW3-12}. The trends in the G^E values somewhat follow the variation in the β^m values, and if both conditions for synergism are considered, the agreement between Motomura's theory and RST is quite satisfying!
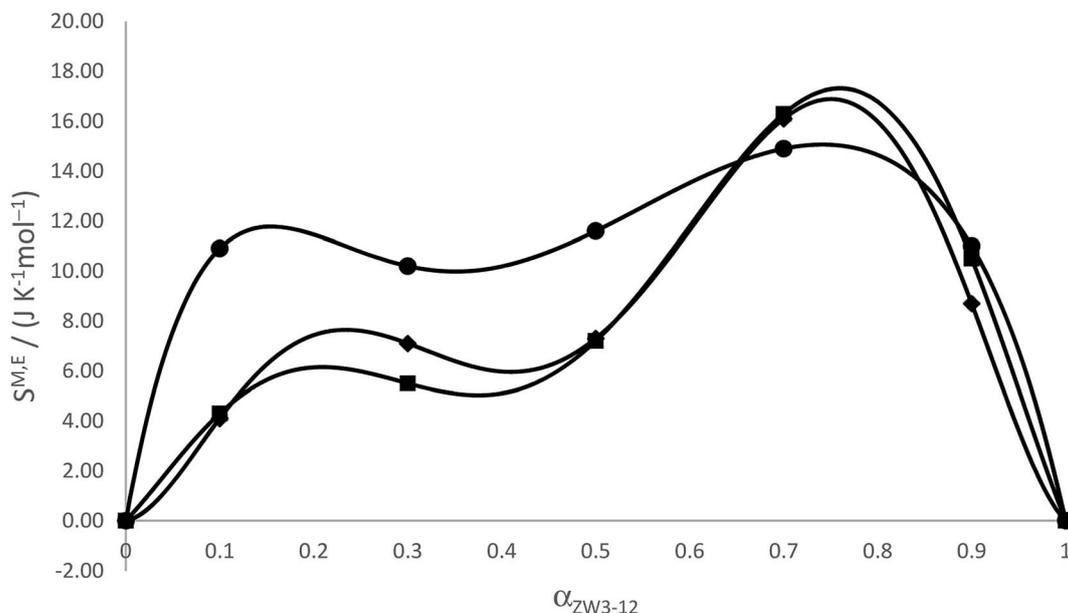

Fig. 7 Excess entropies of mixing from Motomura's theory for ZW3-12/12-*s*-12 system as a function of the mole fraction of zwittergent (α_{ZW3-12}). ● 12-4-12; ◆ 12-5-12; ■ 12-6-12.

An analysis of the results from both RST and Motomura's theory indicates nonideality for all the binary mixed systems and that synergistic interactions are observed, but only in certain compositions of the mixed surfactant system. From our previous paper and the work of Bakshi and Singh, we know that combinations of this zwitterionic surfactant could exhibit strong synergism.[31,74] Surprisingly, although the zwitterionic surfactant possesses a permanent positive charge, when it is transported into the gemini surfactant pseudophases the micellization will still proceed spontaneously ($\Delta_{\mathrm{mic}}G < 0$), even with the significant repulsions that would be experienced in the headgroup regions due to the presence of the permanent positive quaternary ammonium group in the zwittergent. In the case of the 12-4-12 mixed with the zwittergent, the G^{E} values from both theories indicate some destabilization in the mixed micelle *versus* the mixture of the pure surfactant micelles at the same mole fraction. From Motomura's theory, the G^{E} values and the calorimetrically obtained H^{E} values also show the effect of the lengthening spacer. At small amounts of added zwittergent in the case of the 12-4-12 system, the positive charge localized on the quaternary ammonium interacts significantly with the two cationic quaternary ammonium groups on the gemini surfactants. Due to the short average length of the spacer chain (termed d_{S}) *versus* the length where the electrostatic repulsions between the gemini head groups would be minimized (termed d_{T}), the zwittergent will have difficulty mixing with gemini micelles as it is undergoing electrostatic interactions with the gemini headgroups. The increase in the excess entropy at these compositions may indicate that only some of the added zwittergent will form mixed micelles, *i.e.*, the system will contain a large fraction of pure gemini micelles and possibly some pure zwittergent micelles. As the amount of the zwittergent is increased, the excess Gibbs energy, excess enthalpy, and excess entropy values plateau, consistent with a lessening of the electrostatic interactions as the zwittergent molecules replace more gemini molecules in the mixed aggregates. This has been observed in previous zwitterionic/cationic surfactant systems.[74] In all three systems when the mixed micelles are rich with zwitterionic component, the excess enthalpies, Gibbs energies and entropies are close in magnitude, although in the case of the ZW3-12/12-4-12 system, the G^{E} values only become negative at high amounts of added zwittergent, consistent with their synergistic interactions in this composition range.

The incorporation of zwitterionic surfactant monomers into the micelles of gemini surfactants, and their subsequent synergistic mixing, is clearly affected by the spacer length. This is most likely due to the increase in hydrophobicity at the level of the headgroups with the increase in the number of spacer methylene groups, and the change in the distance, d_{S}. Mixed micelle formation is thermodynamically favorable ($\Delta_{\mathrm{mic}}G < 0$), and the variation of the excess thermodynamic parameters of mixing indicate that the surfactants have a greater tendency to synergistically mix at high amounts of zwittergent and longer spacer lengths. At low zwittergent amounts, the steric interactions between the intercharge arms of the two surfactants are likely influencing the ability of the alkyl chains of the surfactants to fold back into the mixed aggregates. This corresponds

well with the observations made by Bakshi and Singh,[74] *i.e.*, increased hydrophobic interactions occur when the dual chains of a gemini amphiphile are packed into a mixed micelle with the single tail of a conventional surfactant. These interactions play a predominant role in the appearance of synergistic interactions.[46,58,74] At $\alpha_{\mathrm{ZW3-12}} = 0.2$, when the excess thermodynamic values plateau for the ZW3-12/12-4-12 system, the tails of the gemini are likely not as prohibited from folding back. The excess thermodynamic properties in all the studied systems are relatively similar at high $\alpha_{\mathrm{ZW3-12}}$ values: the G^{E} values are all negative, and the H^{E} values and S^{E} values are almost identical in value. For the ZW3-12/12-6-12 systems, the excess Gibbs energy is negative over all values of $\alpha_{\mathrm{ZW3-12}}$, indicating the interactions between the headgroups of the two surfactants and the tails are more favourable with the 6 carbon spacer length gemini surfactant. This is again consistent with the increase in d_{S}, *i.e.*, the dual cationic groups of the gemini are able to achieve greater separation which in turn provides room to accommodate the zwittergent head groups with its own cationic group. This increased distance between the quaternary nitrogens in the gemini allows for better packing in the headgroup regions, permitting the folding back of the alkyl chains of both surfactants and increased interactions in the mixed aggregates of the ZW3-12/12-6-12 system.

Conclusions

The mixed micelle formation enthalpies ($\Delta_{\mathrm{mic}}H$ values) were used along with regular solution theory and Motomura's theory to determine excess thermodynamic quantities of the surfactants in the mixed system. The non-zero excess enthalpies of mixed micelle formation increased rapidly as the zwittergent surfactant replaced the gemini surfactant in the ZW3-12/12-4-12 system; the H^{E} values were observed to follow a different trend for both the ZW3-12/12-5-12 and the ZW3-12/12-6-12 systems. The excess thermodynamic properties indicate the mixed micelle formation mixing is strongly dependent on electrostatic interactions and the structure of the surfactants involved, specifically, the length of the tether group for the 12-*s*-12 gemini surfactants. An analysis of the excess thermodynamic properties suggests that the relative contribution of enthalpic and entropic effects to the nonideal behavior for mixed micelles involving gemini surfactants is strongly dependent on the gemini structure. The excess Gibbs energies thus obtained are in excellent agreement with the conclusion of our previous paper concerning the synergistic interactions in these systems, *i.e.*, these systems are not truly synergistic over all compositions. The favourable alkyl tail interactions in these systems, coupled with the repulsive interactions observed between the headgroups in the ZW3-12 and the gemini surfactants, leads to increased hydrophobic interactions in the mixed micelles and greater attractive interactions as the spacer length of the gemini surfactant is increased.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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