

Phase behavior and mixing properties of symmetric gemini surfactant nano structures by quasichemical theory

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ABSTRACT

In the academic and industrial sectors, there has been a significant level of attention directed towards novel surfactants, particularly nano gemini surfactants, owing to their distinctive characteristics in recent times. The utilization of the quasichemical approximation has enabled the determination of phase equilibrium and the mixing properties for solutions of this nature. The Helmholtz free energy, mixing entropy, and mixing energy were ascertained through the variation of hydrophilic and hydrophobic units in nano gemini surfactants. The augmentation of the hydrophilic properties of the nano gemini surfactant has been observed to enhance the reaction of mixing. In turn, there is a reduction in the energy required for mixing. Furthermore, the negative value of the Helmholtz free energy of mixing has been observed to increase. When the hydrophobicity of a nano gemini surfactant increases, a contrary result to previous findings is observed. The mixing entropy remains unaffected by the hydrophobic and hydrophilic units of the nano gemini surfactant. An increase in the hydrophobic tail length of the surfactant leads to a corresponding increase in the two-phase equilibrium region. Conversely, a decrease in the hydrophobic tail length results in a decrease in the two-phase equilibrium region.

Keywords

Nano gemini surfactant; Thermodynamic mixing properties; Phase diagram; Quasichemical theory

1. Introduction

Nano gemini surfactants are composed of a pair of amphiphilic moieties linked by either a hydrophobic or hydrophilic spacer group [1,2]. These compounds have garnered significant attention due to their low CMC values and superior effectiveness in reducing water surface tension compared to conventional surfactants. Their advantageous properties have been well-documented in the literature, as evidenced by the growing interest in this class of compounds [3-7]. Lattice models offer a valuable framework for theoretically approximating thermodynamic properties of amphiphile solutions [8-10]. These models enable analytical simplifications and significantly reduce the computational resources required for calculating

thermodynamic properties. An example of commonly used analytical lattice models is the quasichemical approximation (QCA), which predicts thermodynamic properties and phase diagrams for amphiphile solutions [11]. The estimation of surfactant solution phase behavior through quantitative predictions is a challenging task. The quasichemical approximation has been employed by Larson et al. [12,13], Mackie et al. [14], and Layn et al. [15] to forecast the phase behavior of amphiphile/oil/water solutions. Larson *et al.* and Mackie *et al.* ascertained that the outcomes obtained from the Qualitative Comparative Analysis (QCA) were in proximate concordance with the phase behavior prognosticated by a lattice Monte Carlo (MC) simulation. The phase behavior of the Nano gemini

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surfactant/oil/water system has been examined by Layn et al. through the utilization of lattice Monte Carlo simulation and quasichemical approximation. The predictions of both methods were generally in quantitative agreement. The study conducted by L.A. Rodriguez and colleagues [16,17], investigates the phase behavior and mixing properties of an amphiphile-solvent system. This inquiry was undertaken through the application of lattice theories and Monte Carlo simulations.

The utilization of the QCA is deemed adequate in the accurate prognostication of the characteristics of mixing and phase diagram. Furthermore, the quasichemical approximation has been employed to anticipate the phase behavior of binary mixtures of amphiphiles in solution [18]. Monte Carlo (MC) simulations are a reliable method for determining the precise characteristics of a solution containing lattice amphiphiles. Given the substantial computational requirements of the nano gemini surfactant Monte Carlo simulation method, coupled with the quantitative conformity between the quasichemical theory and the Monte Carlo simulations from prior investigations [12-17], the present work undertook the quasichemical theory for the purpose of predicting the mixing properties and phase diagram of symmetric nano gemini surfactants. Currently, no study has utilized the quasichemical approximation in predicting the thermodynamic mixing properties of nano gemini surfactants. Furthermore, we have conducted an analysis on the impact of tail and head length on the phase behavior of symmetric nano gemini surfactant-solvent systems.

2. Model and Method

2.1. The model

The present investigation aims to conduct a survey pertaining to the thermodynamic characteristics of blending, as well as the patterns observed in the phase behavior of solutions consisting of symmetrical nano gemini surfactants, by utilizing the principles of quasichemical theory. The system consists of a three-dimensional cubic lattice with a coordination number of $Z = 6$, wherein exclusively interactions between neighbors were taken into account. The lattice is entirely occupied by surfactant and water molecules, with each water molecule occupying a solitary lattice site.

The surfactant molecules, on the other hand, occupy the chain of neighboring sites. The nano gemini surfactant chains are denoted as $T_jH_iT_j$, where i ($i > 1$) represents the united head and hydrophilic spacer beads and j ($j > 1$) stands for the tail beads. This work solely focuses on symmetric nano gemini surfactant. A typical nano gemini structure is displayed in Fig.1.



Fig. 1. Gemini surfactant. Yellow circles represent hydrophobic tail segments and green circles represent hydrophilic segments (head or spacer).

2.2. Theoretical Method

The quasichemical approximation has been deemed a more coherent approach for the analysis of amphiphile solutions. The QCA, as explained by Tompa [11], involves the application of nonrandom mixing principles to polymer solutions. In addition, the QCA was expanded to encompass molecules that incorporate diverse types of segments, such as amphiphiles. The QCA postulates that the partition function of the molecules has the potential to be bifurcated into distinct entities, namely an athermal component and a thermal component. The initial category pertains to the input from the combinatorial entropy, while the latter is associated with contributions from the energy and noncombinatorial entropy. The expressions for the energy of mixing in QCA are outlined as follows:

$$\Delta e_{mix} = z\epsilon\kappa HT \sum_{k=1}^2 \frac{q_k \phi_k}{r_k} - z\epsilon\kappa_2 H_2 T_2 \frac{q_2 \phi_2}{r_2} \quad (1)$$

The Helmholtz free energy,

$$\begin{aligned} \Delta f_{mix} &= \Delta f_{mix}^{ath} \\ &+ z/2 \left(H \ln \frac{1 - \kappa T}{H} + T \ln \frac{1 - \kappa H}{T} \right) \\ &- z/2 \sum_{k=1}^2 \left(H_k \ln \frac{1 - \kappa_k T_k}{H_k} \right. \\ &\left. + T_k \ln \frac{1 - \kappa_k H_k}{T_k} \right) \frac{q_k \phi_k}{r_k} \end{aligned} \quad (2)$$

where

$$\begin{aligned} \Delta f_{mix}^{ath} &= \sum_{k=1}^2 \left(\frac{\phi_k}{r_k} \ln \phi_k \right. \\ &\left. + \frac{1}{2} \phi_k \frac{z\phi_k}{r_k} \ln \left(\frac{\xi_k}{\phi_k} \right) \right) \end{aligned} \quad (3)$$

κ is the degree of nonrandomness. The quantities r_k , q_k , H_k and T_k are described in Table 1. H and T are defined by the relationships $H = \sum_{k=1}^2 \xi_k H_k$ and $T = \sum_{k=1}^2 \xi_k T_k$. The determination of the value of κ is achieved through the solution of the quadratic equation.

$$1 - \kappa = \kappa^2 HT (e^{2\varepsilon} - 1) \quad (4)$$

κ_k is acquired by substituting the variables H and T in Equation (4) with H_k and T_k , correspondingly. The surface number of the species k , q_k , is described by the relation $zq_k = r_k(z - 2) + 2$, and ξ_k is the surface fraction of the species k , given by

$$\xi_k = \frac{\frac{q_k \phi_k}{r_k}}{\sum_{k=1}^2 \frac{q_k \phi_k}{r_k}} \quad (5)$$

Table 1. Parameters for the quasichemical approximation for surfactant solutions

Quantity	Solvent	T _i H _i T _j Surfactant
r_k	1	$i + j$
q_k	1	$[r_k(z - 2) + 2]/z$
H_k	1	$[i(z - 2) + 1]/[r_k(z - 2) + 2]$
T_k	0	$[j(z - 2) + 1]/[r_k(z - 2) + 2]$

The designation of $k=1$ pertains to the solvent while $k=2$ pertains to the surfactant. When the magnitudes of energy and free energy of mixing are discerned, it becomes possible to precisely determine the entropy of mixing,

$$\Delta f_{mix} \equiv \Delta e_{mix} - \Delta s_{mix} \quad (6)$$

The chemical potential of component k 's mixing can be acquired through differentiation of Eq. (2) with respect to the quantity of molecules of component k ,

$$\begin{aligned} \frac{(\Delta \mu_{mix})_k}{K_B T} &= \ln \phi_k \\ &+ z/2 q_k \left(\ln \left(\frac{\xi_k}{\phi_k} \right) \right. \\ &+ H_k \ln \left[\frac{H_k(1 - \kappa T)}{H(1 - \kappa_k T_k)} \right] \\ &\left. + T_k \ln \left[\frac{T_k(1 - \kappa H)}{T(1 - \kappa_k H_k)} \right] \right) \end{aligned} \quad (7)$$

The determination of phase behavior is accomplished through the process of equating the chemical potential of every individual component present in one given phase to the corresponding chemical potential of that same component within the other phase.

3. Results and discussion

3.1. Mixing thermodynamic properties

The behavior of the mixture is established through alterations in the molar properties during the mixing process. As presented in Section II, the energies of mixing, derived from Eq. (1), conform to the QCA. Fig. 2 and Fig. 3 depict the values of the energy of mixing for T_jH_iT_j nano gemini surfactant as a function of the nano gemini surfactant volume fraction.

The findings of the mixing energy computations are depicted in Fig. 2 in the context of T_jH₈T_j surfactant systems. With the augmentation of the chain length of nano gemini surfactant, there is a proportional increase in the energy required for the mixing of nano gemini surfactant and solvent.

The impact of the hydrophilic segment length of a T₅H_iT₅ nano gemini surfactant on the mixing energy values is demonstrated in Fig. 3. This phenomenon represents a beneficial process that results in a decrease in the mixing energy.

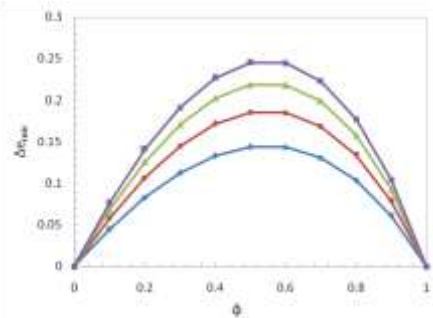


Fig. 2. Mixing energy for T₅H₁S₆H₁T₅ (◆), T₇H₁S₆H₁T₇ (●), T₉H₁S₆H₁T₉ (▲), and T₁₁H₁S₆H₁T₁₁ (■) systems.

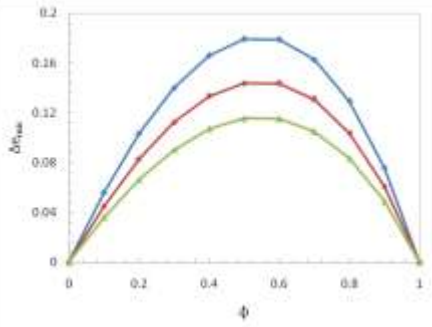


Fig. 3. Mixing energy for $T_5H_1S_4H_1T_5$ (◆), $T_5H_1S_6H_1T_5$ (●), and $T_5H_1S_8H_1T_5$ (▲) systems.

The Helmholtz free energy quantifies the work accomplished on a system under conditions of constant temperature and volume, thereby serving as a useful metric. Fig. 4 and Fig. 5 exhibit the Helmholtz free energy associated with the process of mixing. This measure was ascertained via the employment of QCA theory, whereby Eq. (2) was utilized. As anticipated, a negative change in the process results in a reduction in the negative value of Helmholtz free energy, and conversely, a favorable process leads to an increase in its negative value. For the purpose of examining tail length, the plot in Fig. 4 displays the relationship between the variable of the Δf_{mix} and ϕ , for various magnitudes of tail size. The decrement of the negative value of said quantity is observed with an increase in tail length. A rise in Helmholtz free energy has resulted in the augmentation of the hydrophilic nature of nano gemini(as depicted in Fig. 5).

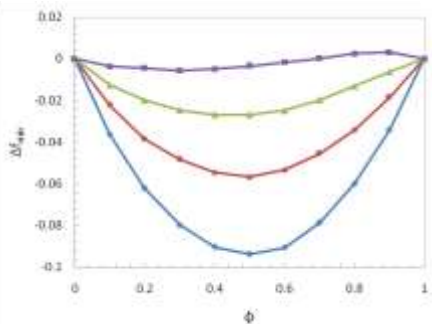


Fig. 4. Helmholtz free energy for $T_5H_1S_6H_1T_5$ (◆), $T_7H_1S_6H_1T_7$ (●), $T_9H_1S_6H_1T_9$ (▲), and $T_{11}H_1S_6H_1T_{11}$ (■) systems.

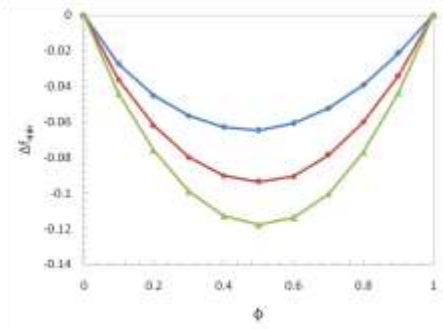


Fig. 5. Helmholtz free energy for $T_5H_1S_4H_1T_5$ (◆), $T_5H_1S_6H_1T_5$ (●), and $T_5H_1S_8H_1T_5$ (▲) systems.

The determination of the Helmholtz free energy and the energy of mixing lead to the inference of the entropy of mixing, which may be derived from Eq. (6). The effects of varying hydrophobic and hydrophilic lengths on the mixing entropy are inconsequential (as depicted in Fig. 6 and Fig. 7).

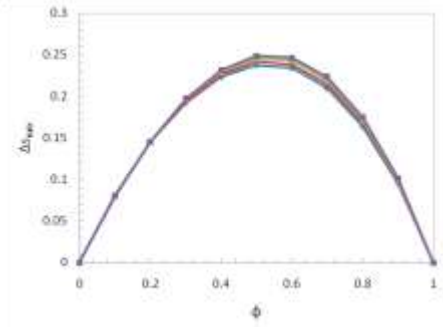


Fig. 6. Mixing entropy for $T_5H_1S_6H_1T_5$ (◆), $T_7H_1S_6H_1T_7$ (●), $T_9H_1S_6H_1T_9$ (▲), and $T_{11}H_1S_6H_1T_{11}$ (■) systems.

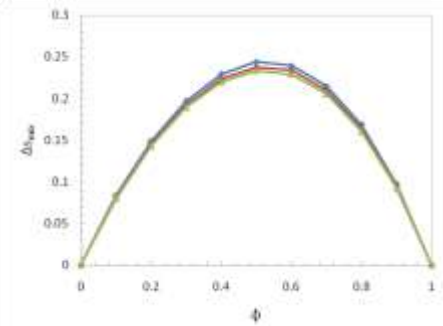


Fig. 7. Mixing entropy for $T_5H_1S_4H_1T_5$ (◆), $T_5H_1S_6H_1T_5$ (●), and $T_5H_1S_8H_1T_5$ (▲) systems.

3.2. Phase behavior

The requirement for achieving equilibrium between two phases in a binary system is articulated by the necessity for equalization of chemical potentials within both phases, that is

$$(\Delta\mu_{mix})_1 = (\Delta\mu_{mix})_1' \quad (8)$$

$$(\Delta\mu_{mix})_2 = (\Delta\mu_{mix})'_2$$

Where, the nomenclature of prime has been embraced to denote a phase of greater concentration. Eq. (7) elucidates the chemical potential of mixing between solvent and molecules that exhibit a linear molecular structure. The phase behavior may be explicated through the replacement of Eq. (7) with Eq. (8). The pair of co-occurring nonlinear equations may be resolved via the application of a numerical technique that exhibits global convergence.

The phase diagram for symmetric nano gemini surfactants has been computed and is depicted in Fig. 8-13. The parameter of dimensionless interaction energy, ε , is associated with the dimensionless temperature through the formulation $T^* = 1/\varepsilon$. Fig. 8-11 depicts the phase characteristics of $T_jH_8T_j$ surfactants, wherein each variant exhibits varying hydrophobic chain lengths. The increase in hydrophobic length leads to an increase in the immiscible limited area.

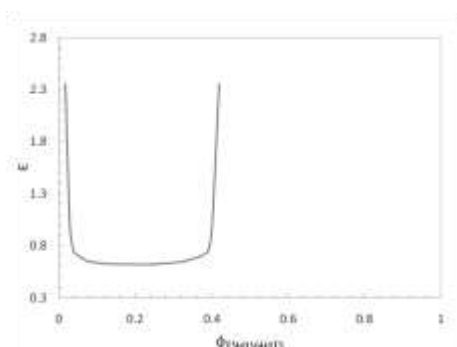


Fig. 8. Phase diagram for $T_5H_1S_6H_1T_5$ in solution.

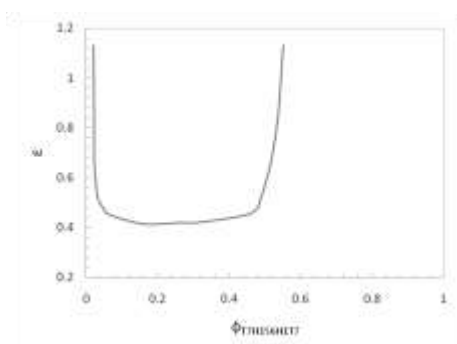


Fig. 9. Phase diagram for $T_7H_1S_6H_1T_7$ in solution.

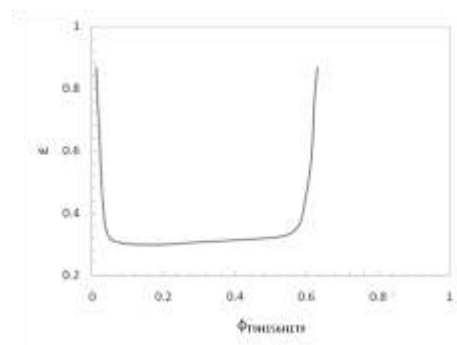


Fig. 10. Phase diagram for $T_9H_1S_6H_1T_9$ in solution.

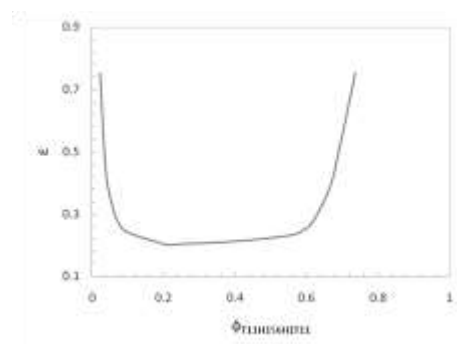


Fig. 11. Phase diagram for $T_{11}H_1S_6H_1T_{11}$ in solution.

When the number of hydrophilic units is increased, there is a corresponding reduction in the immiscible region, as depicted in Fig. 12 and Fig. 13.

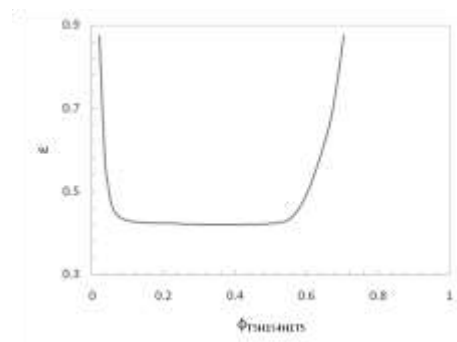


Fig.12. Phase diagram for $T_5H_1S_4H_1T_5$ in solution.

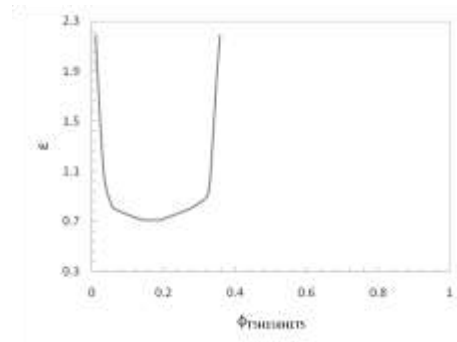


Fig. 13. Phase diagram for $T_5H_1S_8H_1T_5$ in solution.

The critical point can be represented by the minimum value in the above mentioned Figures. The energy of interaction at this particular point is referred to as the critical interaction energy, ϵ_c . The conditions for the critical point are [11]:

$$\frac{\partial(\Delta\mu_{mix})_1}{\partial\phi_2} = 0$$

$$\frac{\partial^2(\Delta\mu_{mix})_1}{\partial\phi_2^2} = 0 \quad (9)$$

Table 2 presents a comprehensive of interaction energy, ϵ_c , and the critical concentration of surfactants, referred to as ϕ_c .

Table 2. Critical points for nano gemini surfactant solutions

Solutions	ϵ_c	ϕ_c
T ₅ H ₁ S ₆ H ₁ T ₅	0.6175	0.1806
T ₇ H ₁ S ₆ H ₁ T ₇	0.4142	0.3215
T ₉ H ₁ S ₆ H ₁ T ₉	0.298	0.4004
T ₁₁ H ₁ S ₆ H ₁ T ₁₁	0.1898	0.5125
T ₅ H ₁ S ₄ H ₁ T ₅	0.4298	0.2805
T ₅ H ₁ S ₈ H ₁ T ₅	0.7092	0.166

4. Conclusions

Theoretical methods were utilized to investigate the phase behavior and mixing properties of symmetric nano gemini surfactants. The variation in the hydrophobic and hydrophilic characteristics of chain-like molecules has been utilized to predict alterations in the energy, Helmholtz free energy and entropy mixing. The examination of the phase behavior of nano gemini surfactants has been conducted via the application of quasichemical theory. As anticipated, the said theory yields satisfactory outcomes through the augmentation of the tails and heads of nano gemini surfactants. Enhancement of the hydrophilic properties of the nano gemini surfactant serves to promote the mixing reaction, leading to a decrease in mixing energy. Moreover, the negative value of the Helmholtz free energy of mixing is observed to increase. When there is an increase in the hydrophilicity of nano Gemini surfactants, a contrasting outcome ensues, which is contrary to previous findings. The presence of hydrophobic and hydrophilic units of a nano gemini surfactant has no discernible impact on the mixing entropy. The two phase equilibrium region exhibited an increase in magnitude with an increase in hydrophobic tail

length, while conversely demonstrating a decrease with an increase in hydrophilic units.

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