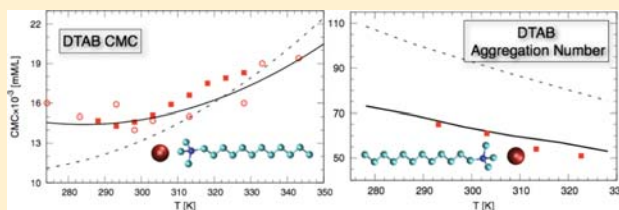


Temperature Effect on Micelle Formation: Molecular Thermodynamic Model Revisited

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ABSTRACT: Temperature affects the aggregation of macromolecules such as surfactants, polymers, and proteins in aqueous solutions. The effect on the critical micelle concentration (CMC) is often nonmonotonic. In this work, the effect of temperature on the micellization of ionic and nonionic surfactants in aqueous solutions is studied using a molecular thermodynamic model. Previous studies based on this technique have predicted monotonic behavior for ionic surfactants. Our investigation shows that the choice of tail transfer energy to describe the hydrophobic effect between the surfactant tails and the polar solvent molecules plays a key role in the predicted CMC. We modify the tail transfer energy by taking into account the effect of the surfactant head on the neighboring methylene group. The modification improves the description of the CMC and the predicted micellar size for aqueous solutions of sodium *n*-alkyl sulfate, dodecyl trimethylammonium bromide (DTAB), and *n*-alkyl polyoxyethylene. The new tail transfer energy describes the nonmonotonic behavior of CMC versus temperature. In the DTAB–water system, we redefine the head size by including the methylene group, next to the nitrogen, in the head. The change in the head size along with our modified tail transfer energy improves the CMC and aggregation size prediction significantly. Tail transfer is a dominant energy contribution in micellar and microemulsion systems. It also promotes the adsorption of surfactants at fluid–fluid interfaces and affects the formation of adsorbed layer at fluid–solid interfaces. Our proposed modifications have direct applications in the thermodynamic modeling of the effect of temperature on molecular aggregation, both in the bulk and at the interfaces.



INTRODUCTION

Temperature may have a profound effect on self-assembled structures in solutions such as micelle formation in aqueous media. Both the critical micelle concentration (CMC) and aggregation number depend on temperature. Experimental data show that the temperature dependency of the CMC is nonmonotonic; there is a minimum in the profile of CMC versus temperature.^{1–5} For ionic surfactants, the minimum is usually around room temperature while for nonionic surfactants it is at higher temperatures. The effect is mostly due to the temperature dependency of the hydrophobic effect⁶ and the interactions between the nonpolar and polar components. Microemulsions containing surfactants, oil, and water also go through dramatic changes in phase and equilibrium state due to temperature.^{7–9} To predict the equilibrium state of microemulsions and micellar solutions with temperature, one may need to improve the thermodynamic model and individual terms in the Gibbs free energy.

Several theoretical attempts have been made to predict the nonmonotonic behavior of CMC versus temperature. Molecular thermodynamic approaches,^{10,11} coarse-grained molecular dynamics (MD),¹² and phenomenological models¹³ have been used to estimate the CMC in aqueous solutions containing either ionic or nonionic surfactants. Previous molecular thermodynamic approaches predict an increase in the CMC with temperature for ionic surfactants¹¹ and a decrease for

nonionic surfactants;¹⁰ neither captures the nonmonotonic behavior. Jusufi et al.¹² used a temperature-dependent Lennard-Jones potential to change the magnitude of the hydrophobic interaction between particles. Their implicit-solvent model predicts a nonmonotonic CMC as a function of temperature, but there are discrepancies between the model predictions and experiments. The implicit-solvent model is applied to both ionic and nonionic surfactants. The phenomenological model introduced by Maibaum et al.¹³ has been calibrated for a specific family of nonionic surfactants. The model reproduces well the temperature dependency of the CMC for this family but fails to predict results for ionic surfactants.

In this article, we use the molecular thermodynamic model for ionic and nonionic surfactants in aqueous solutions to predict the CMC and aggregation number versus temperature at equilibrium. First, the thermodynamic model and temperature dependency in the formulation are explained. The major differences between our investigation and previous works are the (i) modification of the tail transfer energy and (ii) use of a temperature-dependent relation for the interaction parameter of polyoxyethylene (POE) and water in nonionic surfactants. We also modify the head and tail when a charged atom in the head of an ionic surfactant is directly bonded to the carbon in

Received: January 5, 2016

Published: February 8, 2016



the tail. An example is n-alkyl trimethylammonium bromide. In the Results section, we compare the predictions of our model with reported experimental data and the Nagarajan and Ruckenstein model.¹¹

MOLECULAR THERMODYNAMIC MODEL

The molecular thermodynamic model is described in various works.^{11,14,15} We briefly explain the model with emphasis on the temperature dependency of individual energy contributions. The system is composed of N_S surfactant and N_W water molecules at temperature T and pressure p . The Gibbs free energy of the system, G , is

$$G = G_f + G_m \quad (1)$$

where G_f and G_m are the free energies of formation and mixing in the solution, respectively. The free energy of interaction between different species is neglected because we assume a dilute system. The energy of micelle formation is given by

$$G_f = N_W \mu_W^\circ(T, p) + N_{1S} \mu_{1S}^*(T, p) + N_g \mu_g^*(T, p) + N_I^{\text{free}} \mu_I^*(T, p) \quad (2)$$

where N_{1S} , N_g , and N_I^{free} are, respectively, the numbers of monomer surfactant molecules, micelles with g surfactants, and free ions in the solution. We assume that micelles are monodisperse¹¹ and that each micelle is made up of g surfactant molecules. In eq 2, μ_W° , μ_{1S}^* , μ_g^* , and μ_I^* are the chemical potentials of pure water at the standard state, singly dispersed surfactant molecules, micelles of size g , and free ions at infinite dilution, respectively. The species mass balance equations are $N_S = N_{1S} + gN_g$ and $N_I = N_I^{\text{free}} + g\beta N_g$, where β is the degree of counterion binding. The focus of this work is on single-valence surfactant ionic heads and counterions. Therefore, the total number of counterions N_I is equal to the total number of surfactants. The general formulation for ionic surfactants and salts with different valences can be found in ref 15.

For an ideal solution,

$$G_m = k_B T [N_W \ln X_W + N_{1S} \ln X_{1S} + N_g \ln X_g + N_I^{\text{free}} \ln X_I^{\text{free}}] \quad (3)$$

where k_B is the Boltzmann constant and

$$X_j = \frac{N_j}{N_W + N_{1S} + N_g + N_I^{\text{free}}} \quad (4)$$

is the mole fraction of species $j \in \{W, 1S, g, I\}$. A thorough investigation on different mixing models¹⁶ shows that the ideal mixing model for the free energy of mixing can predict CMC very close to the experimental measurements and perform better than other models. The total Gibbs free energy is a function of T , p , N_W , N_S , N_g , β , and g . The independent variables for the minimization of the Gibbs free energy are N_g , β , and g . We collect the terms in G that depend on fixed variables and define G' as

$$G' = G - N_W \mu_W^\circ - N_S \mu_{1S}^* - N_I^{\text{free}} \mu_I^* \quad (5)$$

By substituting eqs 3 and 2 into eq 1 and using the result to simplify eq 5, we arrive at

$$\frac{G'}{k_B T} = \frac{gN_g \Delta \mu_g^*}{k_B T} + N_W \ln X_W + N_{1S} \ln X_{1S} + N_g \ln X_g + N_I^{\text{free}} \ln X_I^{\text{free}} \quad (6)$$

where

$$\Delta \mu_g^* = \frac{1}{g} \mu_g^* - \mu_{1S}^* - \beta \mu_I^* \quad (7)$$

is the free energy change due to the transfer of one surfactant molecule at infinite dilution in the solution to the micelle. $\Delta \mu_g^*$ is the free energy of micelle formation per surfactant molecule, which includes contributions from different energies. Each of these contributions, either explicitly or implicitly, depends on temperature, as will be discussed later in this section. The Gibbs free energy G' of a system without micelles, $N_g = 0$, has only terms from mixing. Thus,

$$\frac{G'}{k_B T} = N_W \ln X_W + N_{1S} \ln X_{1S} + N_I^{\text{free}} \ln X_I^{\text{free}} \quad (8)$$

To determine the state of the system and the minimum in the Gibbs free energy, we minimize eq 5 using the FFSQP algorithm¹⁷ and compare the free energy of the two systems: the one without micelles and the one with N_g micelles of size g .

The free energy of micelle formation includes different energy contributions. Some terms are shared by both ionic and nonionic surfactants, and some terms are specific to each of them. We first present the energies that are specific for ionic surfactants and then explain the ones related to nonionic surfactants with the POE heads.

Ionic Surfactants. Transfer of Surfactant Tail. The largest contribution to the free energy of micelle formation is the energy released due to the transfer of the surfactant n-alkyl tail from the aqueous solution to the hydrocarbon core of the micelle. Experimental data on the solubility of hydrocarbons in water can be used to obtain the tail transfer energy.¹¹ To measure the solubility of hydrocarbons in water, an indirect technique can be used. First, the free energy difference between the hydrocarbon in a gas phase at 1 atm pressure and the hydrocarbon in its saturated state in water is obtained by Henry's constant. Second, the difference in the standard free energies of the hydrocarbon in the gas phase at 1 atm and its pure liquid state is obtained from the vapor pressure data. The relation between the above energies for a hydrocarbon is given by

$$\Delta \mu_h(\text{liquid} \rightarrow \text{aqueous}) = \Delta \mu_h(\text{liquid} \rightarrow \text{gas}) + \Delta \mu_h(\text{gas} \rightarrow \text{aqueous}) \quad (9)$$

$\Delta \mu_h(\text{gas} \rightarrow \text{aqueous})$ is obtained through Henry's constant. We briefly explain the relationship between Henry's constant and the solubility free energy. Consider a system composed of two phases: a gas phase including hydrocarbon gas and water molecules and an aqueous phase consisting of dissolved hydrocarbon and water molecules. The two phases are assumed to be in thermodynamic equilibrium. At equilibrium, the chemical potentials for each component should be equal in both phases

$$\mu_i^{\text{Aq}}(p, T, x) = \mu_i^{\text{G}}(p, T, y) \quad (10)$$

where Aq and G refer to the aqueous and gas phases and $i \in \{w, h\}$ refers to either the solvent (water) molecules or the solute

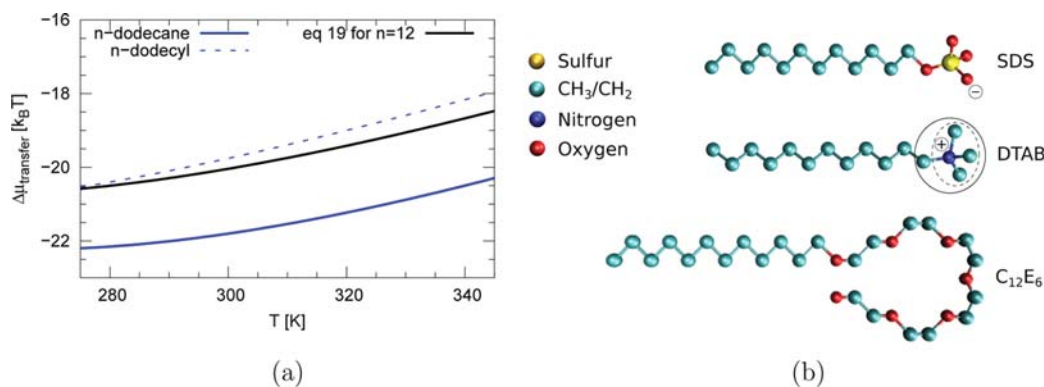


Figure 1. (a) Transfer energy for *n*-dodecane (solid blue) compared to the *n*-dodecyl radical (dashed blue) and the averaged value (solid black) from eq 19 for $n = 12$. (b) Schematic of sodium dodecyl sulfate (SDS), dodecyl trimethylammonium bromide (DTAB), and hexaethylene glycol monododecyl ether, $C_{12}E_6$.

(hydrocarbon) molecules. The mole fractions in the aqueous and gas phases are x and y , respectively. In the aqueous phase,

$$\mu_i^{\text{Aq}}(p, T, x) = \mu_i^{\circ\text{Aq}}(p, T) + RT \ln(\gamma_i x_i) \quad (11)$$

where $\mu_i^{\circ\text{Aq}}$ is the chemical potential of component i at standard state and the argument of the natural logarithm is the liquid phase activity for the same component. For the aqueous phase, the standard state is the nonsymmetric convention in which x_w goes toward 1 so that the solvent obeys Raoult's law, being in the pure state, and x_h goes toward 0, meaning that the solute complies with Henry's law at infinite dilution. In the gas phase,

$$\mu_i^{\text{G}}(p, T, y) = \mu_i^{\circ\text{G}}(T) + RT \ln(py_i \phi_i) \quad (12)$$

where $\mu_i^{\circ\text{G}}$ is the standard state chemical potential of component i in the gas phase. For the gas phase, the standard state is the ideal gas state at temperature T and $p = 1$ atm. The argument of the natural logarithm in eq 12 is the gas phase fugacity. By equating eqs 11 and 12 for hydrocarbon,

$$\Delta\mu_h(p, T)(\text{gas} \rightarrow \text{aqueous}) = RT \ln\left(\frac{py_h \phi_h}{\gamma_h x_h}\right) \quad (13)$$

The argument of the natural logarithm is the Henry's law constant for the solute (hydrocarbon) in the solvent (water), $\mathcal{H}_{h,w}(p, T)$. Therefore, one can relate the free energy of solubility of a gas hydrocarbon in water to Henry's constant,

$$\Delta\mu_h(p, T)(\text{gas} \rightarrow \text{aqueous}) = RT \ln \mathcal{H}_{h,w}(p, T) \quad (14)$$

With accurate values of $\mathcal{H}_{h,w}$ at constant pressure and various temperatures, one obtains the temperature dependency of the free energy of solubility through eq 14. The data for Henry's constant can then be fitted to an equation which is a function of temperature and gives the free energy of dissolving the gas in water. If the equation is differentiated, then the enthalpy and entropy of the process are obtained. The temperature function can be a simple polynomial. However, it has been shown that including the $\ln T$ term leads to a better-behaved function and improves the fit to experimental data.¹⁸ Using the free energy data for the solubility of different alkane chains (methane to *n*-octane),¹⁸ one can estimate methyl and methylene group contributions in the free energy of solubility and their temperature dependencies.

Vapor pressure data for alkanes provide the values for $\Delta\mu_i(p, T)(\text{liquid} \rightarrow \text{gas})$ at standard state.¹¹ Then, we can obtain

$\Delta\mu_h(\text{liquid} \rightarrow \text{aqueous})$ by using eq 9. The final form of the temperature function that gives the energy of transferring one methylene group from the aqueous solution to the liquid hydrocarbon state is¹¹

$$\frac{(\Delta\mu_g)_{\text{CH}_2}}{k_B T} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056T \quad (15)$$

and the corresponding expression for one methyl group is¹¹

$$\frac{(\Delta\mu_g)_{\text{CH}_3}}{k_B T} = 3.38 \ln T + \frac{4064}{T} - 44.13 - 0.02595T \quad (16)$$

For *n*-alkane chains, the transfer energy is obtained by including two methyl groups and $(n - 2)$ methylene groups as

$$\frac{(\Delta\mu_g)_{\text{tr-alkane}}}{k_B T} = (n - 2) \frac{(\Delta\mu_g)_{\text{CH}_2}}{k_B T} + 2 \frac{(\Delta\mu_g)_{\text{CH}_3}}{k_B T} \quad (17)$$

We note that the experimental data that are used to obtain the methyl and methylene contributions are deduced from complete *n*-alkane chains. The tail transfer energy for *n*-alkyl chains can be obtained by adding the energy for one methyl group and $(n - 1)$ methylene groups. Thus,

$$\frac{(\Delta\mu_g)_{\text{tr-alkyl}}}{k_B T} = (n - 1) \frac{(\Delta\mu_g)_{\text{CH}_2}}{k_B T} + \frac{(\Delta\mu_g)_{\text{CH}_3}}{k_B T} \quad (18)$$

All past studies based on the model developed by Nagarajan and co-workers have used eq 18 for the transfer energy of an *n*-alkyl tail of a surfactant. In this approach, the last methylene group is considered to be the same as other methylene groups in the alkyl chain. In reality, this is clearly not the case. The last carbon pairs its fourth electron with the surfactant head, and the tail is not a radical molecule. In a different treatment of tail transfer energy, Blankschtein and co-workers have considered the tail to be an alkane with $(n - 1)$ carbons and the surfactant hydrophilic headgroup plus the CH_2 group adjacent to it to be the head. They have applied this approach for both ionic and nonionic surfactants. Blankschtein's thermodynamic model is almost the same as Nagarajan's model in concept. However, there are some differences in details that do not allow for a point-to-point comparison. Blankschtein and co-workers studied only the effect of temperature in aqueous solutions of nonionic surfactants.

We propose a new expression for the tail transfer energy and show that this new expression improves the predictions of the thermodynamic model for both ionic and nonionic surfactants. The suggested expression is given by

$$\frac{(\Delta\mu_g)_{tr}}{k_B T} = \frac{(\Delta\mu_g)_{tr-alkyl}}{k_B T} \Big|_{n-1} + \frac{1}{2} \frac{(\Delta\mu_g)_{CH_3}}{k_B T} \quad (19)$$

which includes the transfer energy of an imaginary chain composed of an alkyl with $(n - 1)$ carbon atoms plus half of a methyl group. The modification is based on two considerations: (i) the last carbon in the tail chain, attached to the surfactant head, is not free like a radical molecule and (ii) the interface between water and the micelle hydrocarbon core fluctuates on the order of 0.1–0.2 nm, which is about the length of one carbon–carbon bond.¹⁹ Let us consider the case for $n = 12$. Figure 1(a) shows the temperature dependence of the transfer energy for n -dodecane, the n -dodecyl chain, and the plot from eq 19 for $n = 12$. Note that the absolute value of the transfer energy from eq 19 is larger than the transfer energy from eq 18 for $n = 12$. The distinction between n -dodecyl and n -dodecane is one hydrogen, but the difference in their transfer energy starts from $\sim 1.5k_B T$ at $T = 275$ K and grows to $\sim 2k_B T$ at $T = 343$ K. There is a large effect of a single hydrogen atom on the absolute value of tail transfer energy. When a surfactant from the bulk solution becomes part of a micelle, the head also transfers with the tail. One way to take the head into account is to consider it to be a hydrogen atom since this is the only available solubility data. So the last carbon in the tail may have properties closer to those of CH_3 rather than CH_2 . The second consideration we mentioned is that the surface of the hydrophobic core fluctuates in the range of one carbon–carbon bond length. Therefore, the imaginary methyl-like group moves back and forth between the aqueous solution and the micelle hydrophobic core. This justifies using half of the CH_3 contribution in eq 19.

In essence, what we suggest is that the carbon attached to the surfactant headgroup cannot be counted as a methylene group in the tail transfer energy because it is covalently bonded to the headgroup and shares electrons with it. As a first (and simplest) approximation, we can consider it to be a methyl-like group with half of the contribution because it moves back and forth between the solution and hydrocarbon core and generates the fluctuations of the micelle surface.

In this study, we apply our model to the family of anionic sodium n -alkyl sulfate, cationic DTAB, and the family of nonionic surfactants with POE headgroups. There is a distinct difference between DTAB and the other two. As is shown in Figure 1(b), for the SDS molecule there is a sulfur and an oxygen atom between the oxygen with a negative charge and the immediate carbon atom attached to the head. For DTAB, the last carbon atom of the tail is directly bonded to the nitrogen which has a positive charge. The distance between the charged atom and the last carbon in the tail has a profound effect on how part of the core of the micelle can be wetted by water molecules. In DTAB, the charge on the nitrogen has a strong impact on the last carbon and changes its electron cloud distribution. For SDS, the distance between the charged oxygen and the last carbon dilutes the effect of charge. In $C_{12}E_6$, no charge is involved. The above explanation leads us to treat DTAB differently. We include the last carbon of the alkyl chain in the head rather than in the tail. Our proposed head and the one considered by others are circled by solid and dashed lines

in Figure 1(b), respectively. Basically, we consider a larger head and a shorter tail for DTAB because the nitrogen charge directly affects the carbon atoms attached to it. Our modification is supported by a recent finding.²⁰ Long et al. have used Raman spectroscopy to study the hydration of the hydrocarbon core of micelles. They studied surfactants with cationic trimethylammonium headgroups. The tail is an alkyl chain with different lengths. Their results show that water molecules penetrate the hydrophobic core and some methylene group adjacent to the head are wetted by water. Their observation is in line with the modification we apply to DTAB.

Deformation of the Surfactant Tail. The deformation energy $(\Delta\mu_g)_{def}$ as suggested in ref 11, is

$$\frac{(\Delta\mu_g)_{def}}{k_B T} = \frac{9P\pi^2 R_c^2}{80 l_{ST}L} \quad (20)$$

where P is the packing parameter for spherical micelles defined by the properties of the surfactant and the micelle as ν_{ST}/aR_c . R_c and a are the hydrocarbon core radius and the surface area of the core per surfactant molecule, respectively. ν_{ST} is the volume and l_{ST} is the extended length of the surfactant tail. $L = 0.46$ nm is the length of the segments in the tail.¹¹ $(\Delta\mu_g)_{def}$ does not explicitly depend on the temperature. However, as the size of the aggregate changes with temperature due to other contributions, a varies and so does the deformation energy. The energy of deformation is small compared to other contributions.

Formation of the Micelle Core–Water Interface. The formation of the hydrocarbon core of the micelle introduces an interface between the core and the surrounding aqueous medium. The formation of this interface is an important contribution to the micelle formation energy; its magnitude is the second largest after the tail transfer energy, and it promotes the formation of larger aggregates since it decreases as g increases. The energy of interface formation can be obtained from

$$\frac{(\Delta\mu_g)_{int}}{k_B T} = \frac{\sigma_{agg}}{k_B T} (a - a_0) \quad (21)$$

where σ_{agg} is the interfacial tension between the hydrocarbon core and aqueous solution. a_0 is the interface area that is covered by the surfactant head and counterions that are absorbed at the micelle interface,

$$a_0 = a_s + a_l \beta \quad (22)$$

In eq 22, a_s and a_l are the cross-sectional areas of the surfactant head and counterion, respectively. The radii used in our study are listed in Table 1. In eq 21, temperature appears implicitly through σ_{agg} , which is an explicit function of temperature.¹⁴ As the size of the micelle changes with temperature due to other

Table 1. Dispersion Coefficients and Radii of Counterions and Surfactant Heads Used in the Calculations^a

	ions			
	Na ⁺	Br ⁻	SO ₄ ⁻	Me ₄ N ⁺
dispersion coefficient [10^{-50} J m ³]	0.398	-1.165	-3.205	4.44
bare radius [nm]	0.067	0.216	0.281	0.272

^aDispersion coefficients are calculated on the basis of the method in ref 15 except for the dispersion coefficient for Me₄N⁺, which is from ref 21. Radii are from ref 22.

energy contributions, a will vary. Thus, temperature enters eq 21 implicitly as well as explicitly.

Headgroup Steric Interactions. In a micelle, the polar heads of the surfactants and adsorbed counterions are on the surface of the micelle, and as they get close, steric interactions between them arise. The simplest way to account for these repulsive interactions is to use¹¹

$$\frac{(\Delta\mu_g)_{st}}{k_B T} = -(1 + \beta) \ln\left(1 - \frac{a_0}{a}\right) \quad (23)$$

Temperature is implicitly accounted for through a in steric interactions.

Ionic Interactions. A new approach introduced by Lukanov and Firoozabadi¹⁵ takes into account the ionic free energy between the micelle surface and the double layer around it by solving the Poisson–Boltzmann equation with dispersion potentials. In our study, we use the same technique with the details explained in ref 15. We should note that parameters such as dispersion coefficients and dielectric constants depend weakly on temperature. The temperature dependency of the ionic free energy may not be strong. Dispersion coefficients used in our study are listed in Table 1.

Headgroup and Counterion Mixing Entropy. A small contribution to the free energy of micelle formation is from the mixing of headgroups and counterions at the interface of the micelle,

$$\frac{(\Delta\mu_g)_{ent}}{k_B T} = \ln\left(\frac{1}{1 + \beta}\right) + \beta \ln\left(\frac{\beta}{1 + \beta}\right) \quad (24)$$

Nonionic Surfactants. Tail transfer and tail deformation energies appear as part of the free energy in both nonionic and ionic surfactants. The steric and interface formation energies need modification for nonionic surfactants with the POE headgroups. There are also specific interactions describing the polymer-like behavior of POE heads that we explain in this section.

Headgroup Steric Interactions. For n -alkyl polyoxyethylene surfactants (C_nE_x), the size of the head depends on the number of oxyethylene units in the head, E_x ,

$$a_s = \frac{E_x v_E}{l} \quad (25)$$

where $l = 0.503(E_x - 1)^{0.5}$ nm is the length of a random coil of volume $E_x v_E$.²³ We note that the random coil model is proposed for $8 \leq E_x \leq 65$. Here, we use the same model for $E_x = 4, 6,$ and 8 . Each oxyethylene unit has a volume of 0.063 nm^3 . The head size varies with temperature as the hydration number changes. We adopt the formula suggested by Puvvada and Blankshtein¹⁰ to account for temperature variations of the headgroup size,

$$a_s(T) = a_s[1 - H(T - 298.15)] \quad (26)$$

where H is estimated to be 0.0075 K^{-1} . Equation 26 gives the average head size and can be used in eq 23 as a_0 to calculate the steric energy.

Headgroup Mixing in the Hydrophilic Region of the Micelle. The polymer-like heads mix with water molecules in the hydrophilic region of the micelle. To estimate the energy of mixing, a new independent variable D is introduced as the thickness of the hydrophilic region and is used to estimate the concentration of heads in the hydrophilic region,

$$\phi = \frac{E_x v_E}{Da} \quad (27)$$

This concentration is obtained by assuming a nonuniform distribution of head chains¹¹ in the hydrophilic region. The same assumption is used to find the headgroup mixing energy as

$$\frac{(\Delta\mu_g)_{mix}}{k_B T} = \frac{\phi E_x v_E}{L^3} \left(\frac{0.5 - \chi_{WE}}{1 + D/R_c} \right) \quad (28)$$

where χ_{WE} is the water–POE interaction parameter which depends on temperature. This dependency is accounted for by²⁴

$$\chi_{WE} = 1.2056 - 260.69/T \quad (29)$$

Headgroup Deformation in the Hydrophilic Region of the Micelle. Using a nonuniform concentration of the heads and uniform deformation along the chain length, one obtains¹¹

$$\frac{(\Delta\mu_g)_{def-h}}{k_B T} = \frac{1}{2} \left[\frac{D^2 L}{E_x v_E} + \frac{2(E_x v_E)^{1/2}}{DL^{1/2}} - 3 \right] \quad (30)$$

Formation of a Hydrophobic Core–Hydrophilic Region Interface. Equation 21 remains valid for the energy of interface formation for nonionic surfactants, but σ_{agg} should be modified for nonionic surfactants with the POE head because the interface is between a phase made of hydrocarbon tails and another made of POE and water. Therefore, the composition of the hydrophilic region at the position of the interface determines the interfacial tension along with other parameters. To find the concentration of the polymer segments at the interface, ϕ_s , we solve the following implicit equation¹¹

$$\ln \frac{(\phi_s/\phi)^{L^3/E_x v_E}}{(1 - \phi_s)/(1 - \phi)} = \frac{\sigma_{SW} - \sigma_{SE}}{k_B T} v_s^{2/3} + \frac{3}{4} \chi_{WE} (1 - 2\phi) - \frac{1}{2} \chi_{WE} (1 - 2\phi_s) \quad (31)$$

Interfacial tensions σ_{SE} and σ_{SW} are between the surfactant hydrocarbon tails and POE heads and water molecules, respectively. σ_{SE} and σ_{SW} depend on temperature and can be estimated from experimental data as described in refs 11 and 14, respectively. The overall interfacial tension σ_{agg} can be obtained from¹¹

$$\frac{\sigma_{agg} - \sigma_{SW}}{k_B T} v_s^{2/3} = \ln\left(\frac{1 - \phi_s}{1 - \phi}\right) + \left(1 - \frac{L^3}{E_x v_E}\right) (\phi_s - \phi) + \chi_{WE} \left[\frac{1}{2} \phi_s^2 - \frac{3}{4} \phi^2 \right] \quad (32)$$

A summation of all free energies replaces the free energy of micellization in eq 6. We then find a set of independent variables that minimize G' in eq 6 and compare the minimum with the energy of a system with no micelles from eq 8. As formulated above, for ionic and nonionic surfactants the sets of independent variables for minimization are $\{g, \beta, N_g\}$ and $\{g, N_g, D\}$, respectively.

RESULTS

In this section, we present results for the temperature dependency of CMC and the aggregation number. We have modified the tail transfer energy to improve the predictions. We

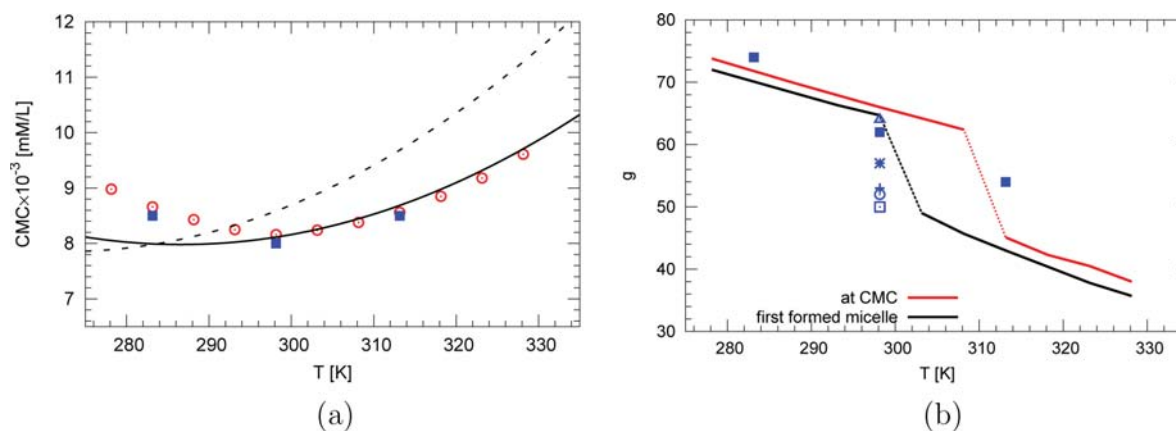


Figure 2. (a) Temperature dependence of the CMC for SDS in water. Experimental data are shown by circles² and squares.⁴ Predictions of the NR and modified models are plotted by dashed and solid lines, respectively. (b) Temperature dependence of the aggregation number for SDS in water. Solid red and black lines are predictions of the model for the aggregation size at the CMC and of the first formed micelle, respectively. Filled squares are from ref 4, and other experimental data are from ref 15 and references therein.

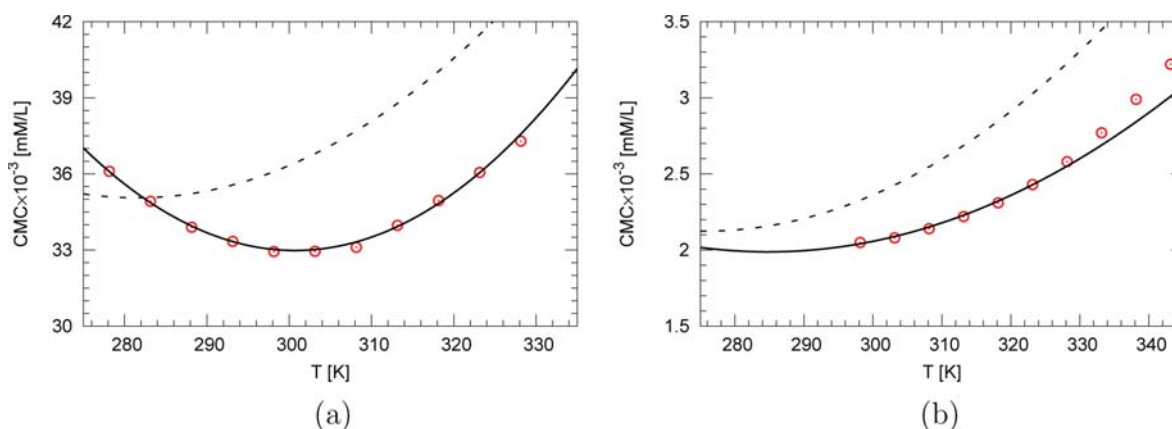


Figure 3. Temperature dependence of the CMC for (a) the SDeS and (b) the STS in water. Experimental data are shown by circles.² Predictions of the NR and modified models are plotted by dashed and solid lines, respectively.

compare the results of the modified model with experimental data and the model of Nagarajan and Ruckenstein¹¹ (NR model).

Ionic Surfactants. Data on the effect of temperature on the CMC and aggregation numbers have been reported for a number of surfactants, mainly in the sodium *n*-alkyl sulfate family. SDS is the most widely studied. Figure 2(a) shows the variation of the CMC with temperature for SDS. Experimental data of CMC show a clear minimum around room temperature. A comparison of our modified model and the NR model shows that the new tail transfer energy allows us to predict a minimum for the CMC. The NR model predicts that the CMC always increases with temperature while our modified model shows a decrease with increasing temperature for $T < 290$ K. The modified model also gives a better prediction of the CMC at room and higher temperatures.

Aggregation numbers for SDS from our modified model and experiments are shown in Figure 2(b). The difference between the two predicted lines by the model is that one of them represents the size of the first formed micelle in the system and the other shows the aggregation number at the CMC. Usually, g at the CMC is slightly larger than the size of the first formed micelle. For SDS, the thermodynamic model predicts a window of 10° ($300 \text{ K} < T < 310 \text{ K}$) where there is a large difference

between the two sizes. The reported experimental data at room temperature vary widely near this window. A set of data for three temperatures including room temperature are also presented in Figure 2(b). It shows a monotonic decrease in aggregation size with increasing temperature; the model predicts the same trend.

We also compare the predictions of the model with CMC data from the literature for sodium decyl sulfate (SDeS) and tetradecyl sulfate (STS). The results are shown in Figure 3(a,b) for SDeS and STS, respectively. In both, the experimental data are well reproduced by our modified model while the results of the NR model show a significant difference. In SDeS, the minimum in the CMC is accurately captured by the modified model. If one compares the minima of CMCs for the sodium *n*-alkyl sulfate family from the model prediction, then it is notable that they move toward higher temperatures as the tail length decreases. The prediction is in line with experiment,²⁵ although the observed shift is smaller for experimental data.

We also validate our modified model by comparing predicted CMC and aggregation numbers with experimental data for dodecyl trimethylammonium bromide (DTAB). We note that in a previous study on the thermodynamic modeling of DTAB in aqueous solution¹⁴ the head of the surfactant is considered to be trimethylammonium. Here, we add the immediate

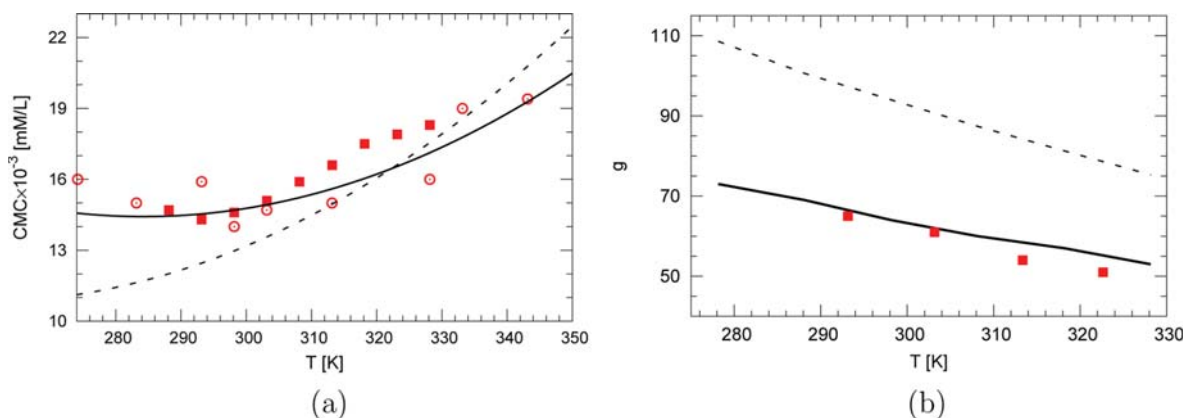


Figure 4. Temperature dependence of the (a) CMC and (b) aggregation number for DTAB in water. Predictions of the NR and modified models are plotted by dashed and solid lines, respectively. In (a), experimental data are shown by circles¹ and squares.³ Experimental data are shown by squares in (b) and are from ref 26.

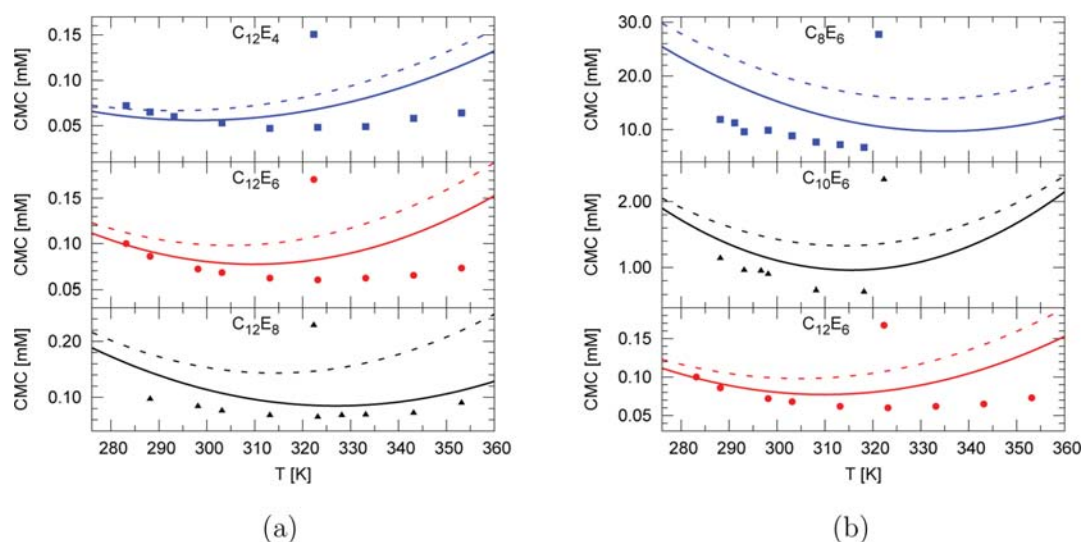


Figure 5. Temperature dependence of the CMC for n-alkyl polyoxyethylene surfactants in water: (a) $C_{12}E_x$ and (b) C_nE_6 families. Predictions of the NR model combined with eq 29 and our modified model are plotted by dashed and solid lines, respectively. Experimental data shown by circles, squares, and triangles are from ref 1.

methylene group after the nitrogen to the head and consider the tail to have 11 carbon atoms. In this way, the size of the head is closer to that of tetramethylammonium. For other parameters such as dispersion coefficients, we use values for tetramethylammonium as well. The temperature dependence of the CMC and aggregation numbers for DTAB are shown in Figure 4(a,b), respectively. The experimental data for the CMC are well reproduced by our modified model, and aggregation numbers are very well matched because of the new definition for the DTAB head.

Nonionic Surfactants. For nonionic surfactants with POE headgroups, the interplay between the temperature dependence of the tail transfer energy and the interaction parameter determines the minimum in the CMC. We examine the model for two classes of surfactants. In the first class (CI), the number of carbon atoms in the tail is constant and the size of the head increases; we choose dodecyl as the tail and examine headgroups with 4, 6, and 8 POE groups. For the second class (CII), the size of the head is fixed and the number of carbon atoms varies in the tail; we pick a head with 6 POE groups and examine tails with 8, 10, and 12 carbon atoms.

Nagarajan and Ruckenstein¹¹ have not studied the temperature effect on the micellization of nonionic surfactants. In this section, we combine the NR model with eq 29 to calculate the CMC.

Figure 5(a,b) shows the temperature dependence of the CMC for CI and CII surfactants, respectively. For CI, the general conclusion is that the model prediction improves when the size of the head increases. This is expected because the model considers the head to be a polymer chain and small values for E_x may not justify this assumption. For a large E_x , our modified model gives a better estimation for the CMC compared with the NR model. It correctly follows the nonmonotonic trend and predicts the minimum. In CII, we pick $E_x = 6$. The estimations from our modified model are closer to experimental data than those from the NR model. The predictions of our model show that the minimum in the CMC moves to higher temperatures with varying numbers of carbon atoms in the tail. There are no CMC measurements for the desired range of temperatures (except for $C_{12}E_6$), so a comparison with theory is not possible.

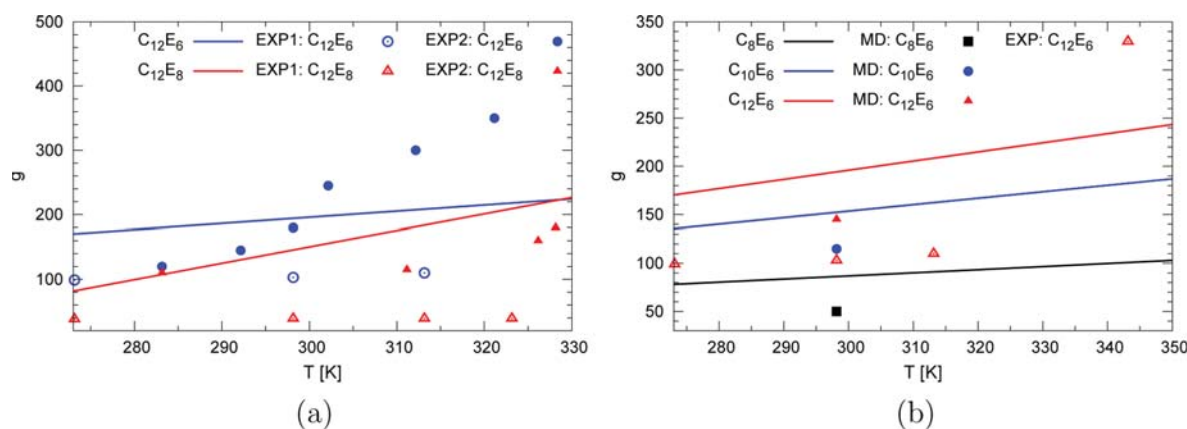


Figure 6. Temperature dependence of the aggregation number for n-alkyl polyoxyethylene surfactants in water: (a) $C_{12}E_x$ and (b) C_nE_6 families. Solid lines are the predictions of this work. Experimental data in (a) which are shown by open symbols are from ref 27, and filled symbols are from ref 28. In (b), filled symbols are the results of MD simulations from ref 12, and other data are from ref 27.

Most of the data on the aggregation number for nonionic surfactants with the POE headgroup are at room temperature. There are a few measurements for other temperatures. However, the data vary widely and in some cases there is a 3-fold difference between measurements by different authors. We plot the predictions of our modified model and reported experimental data for $C_{12}E_6$ and $C_{12}E_8$ together in Figure 6(a). Despite the discrepancy among the experimental data, the overall trend is that g increases with temperature and decreases with the increase in E_x when the number of carbon atoms in the tail is constant. Our model predicts the same behavior. Figure 6(b) shows our predictions for the aggregation number of CII surfactants. The experimental data is for $C_{12}E_6$. We also show the results of a coarse-grained MD model at room temperature. Our results at room temperature are in line with MD simulations; surfactants with longer tails form larger micelles. The model also predicts an increase in the slope of change in g when the number of carbon atoms in the tail increases.

CONCLUSIONS

Modification of the tail transfer energy in the molecular thermodynamic model improves the predictions of the temperature effect for the CMC of ionic and nonionic surfactants. The tail transfer energy is a function of temperature and has a profound effect on the onset of micellization which defines the CMC. The temperature effect emerges in systems where one of the bulk phases is water and hydrophobicity promotes the self-assembly of structures. Temperature has no effect on systems such as reverse micelles where water is present in trace amounts and driving forces other than hydrophobicity play a role in structure formation.²⁹ In several previous studies,^{11,14,15} the tail transfer energy is calculated by assuming that the tail consists of one methyl and $(n - 1)$ methylene groups. This approach happens to be accurate enough near room temperature but does not predict the temperature dependency of the CMC and the minimum reported in the literature for ionic surfactants. We modify the tail transfer energy by using an alkyl chain with one less carbon attached to a methyl-like group with the half contribution presented by eq 19. Determining the exact contribution of the methylene group closest to the surfactant headgroup is challenging and may require ab initio calculations of the electron distribution and covalent bonding near the headgroup.

The modified model used here can predict the minimum in the CMC data. We believe that our proposed modification for the tail transfer energy is justified because (i) the solubility data are for complete alkane chains and not for alkyls and the last carbon in the tail, attached to the head, is not a radical but is covalently bonded to the head, more like a methyl rather than a methylene, and (ii) experimental measurements show that the interface between the head of the surfactants at the surface of the micelle and its core fluctuates with an amplitude as large as one carbon–carbon bond.¹⁹

The second modification is proposed for headgroups such as trimethylammonium where the charged atom, here the nitrogen, is directly connected to the last carbon. In this case, the electron distribution of the last carbon is affected by the charged atom. We include the methylene group in the head rather than leave it in the tail. Experimental measurements support the proposed modification.²⁰

Our model improves the predictions from the molecular thermodynamic model, which is a valuable tool for studying micellar and microemulsion systems. The microemulsion phase behavior is quite sensitive to temperature, and a thermodynamic model to reproduce the temperature-dependent trends would be of practical interest. Tail transfer energy is the dominant contribution in the adsorption of surfactants at fluid–fluid interfaces. It also plays a role in the adsorption of surfactants at fluid–solid interfaces. Therefore, any modification in transfer energy is expected to improve adsorption modeling. Molecular thermodynamic modeling is also more cost-effective than molecular dynamics simulations, which are better suited to detailed structural analysis.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the member companies of the Reservoir Engineering Research Institute (RERI) for their financial support.

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