G_{mic}-SAFT Type Equation of State for Aqueous Nonionic Surfactants

Manette J. Macias
Chemistry B.S., Forensic Science B.S.
Faculty Mentor: Dr. Art Gow

Abstract

This project served to construct a new approach for aqueous nonionic surfactant solutions that combined a popular molecular thermodynamic model of micellization with a specialized version of the SAFT equation of state designed for mixtures of micellar aggregates, surfactant monomers and water. This G_{mic} model gives accurate estimates of several features of the micellar solution. The limitation of the G_{mic} expression occurs when combined with a thermodynamic framework, including athermal mixing and mean field interaction between species, yields an empirical model for description of multiple liquid phase behavior of these systems. To overcome this limitation, the G_{mic} model was linked to the specialized SAFT-type equation of state specially designed for micellar systems that accounts for repulsion and dispersion between a variety of different size or shape aggregates, chain molecule monomers and water, modeled as associating hard-spheres. This new SAFT-type equation of state is solved simultaneously with the G_{mic} model to determine ΔG_{mix} versus total surfactant mole fraction to identify the existence of two liquid phases and their composition where present and the osmotic pressure and compressibility of the solution. Data from aqueous nonionic surfactants from the polyoxyethylene glycol monoether family to illustrate key findings from the approach.

Introduction

This project was aimed to develop of an equation of state for particular complex fluids, nonionic surfactants, in water that work with the Gibbs free energy equation. The equation, when properly constructed would enable rapid and accurate screening of micelles by their physical and thermophysical properties and is applicable to scholarly and industrial designs.

Standardization of calculations and analysis in the scholarly and industrial chemical engineering community inspired this research project involving complex fluids and their use in a novel form of equation of state. Complex fluids such as surfactants, molecules composed of polar head groups and nonpolar tails, are currently increasing in demand under this standardization for use in new materials and process design. Surfactant molecules consist of hydrophilic head groups and hydrophobic tails, which generally undergo self-assembly (micellization) above a certain threshold of concentration in water as seen in Figure 1. This happens in order to reduce contact of the hydrocarbon chains comprising the tail with water to form disk, rod, or sphere shape clusters known as micelles.
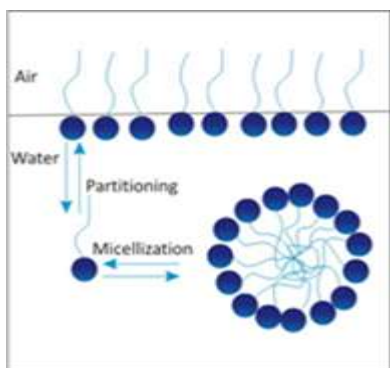

Figure 1: Example of micellization process

Previous research has been done to characterize the effects of several factors impacting the micellization process, such as: hydrophilic and hydrophobic chain lengths, and temperature and pressure on aggregate distribution, which is the size and shape of formed micelles. Simple quantitative models of micellization were advanced in these previous works, but the work of Blanckstein and coworkers is the most comprehensive account of the key microscopic effects including repulsion of hydrocarbon chains and water, hydrocarbon-water interface formation, hydrocarbon chain packing within the formed micellar core and steric head group repulsions. However, these models use an empirical mean-field term that accounts for micellar interactions that drive phase separation.

Equations of State (EOS) are mathematical relationships between the measurable variables of a system: pressure, temperature, and volume. EOS' allow scientists and engineers to predict properties for substances in various mixtures of conditions and/or settings without having to actually perform an experiment or obtain pre-existing data from literature. There are currently many types of these equations of state available that accurately predict data for several classes of simple fluids. However, there are presently very few of these models available for complex surfactant molecules, the type that form micelles. These available models are incapable of giving much of the desired detailed micellar information such as size distribution and shape of aggregates. An ideal approach to the issues of phase separation and complex models was to combine the detailed microscopic modeling of surfactant systems of Blanckstein and Coworkers[1] with a SAFT-EOS framework for description of multiple phase systems.

Methodology/Results

Overall the project followed traditional formation for an equation of state that included repulsive, association, and dispersive terms. Constants were considered in this equation that were fit to each term, given a set of derived parameters and their effect in varying aqueous surfactant systems. Dispersive forces were anticipated necessary and association forces were also expected to affect the other

terms as well. Repulsive terms are not dispersive force dependent and may not cause phase splitting on its own. It was expected the association term would negate repulsive effects. With these forces acting together, phase splitting was included in the anticipated results. In order to properly these effects as close as possible data from a nonionic surfactant was used. This surfactant was a neutral family and would not directly affect the terms of the equation being formed as an ionic, anionic, or zwitter-ionic surfactant would.

The project began with a primary set of equations beginning with the change in Gibbs free energy of mixing,

$$\Delta G_{Mix} = G - x_1 G_1 - x_2 G_2$$

where the x_1 and x_2 are the concentration of surfactant and water respectively. Two equations relating to the Gibbs free energy equation, Helmholtz free energy equation and the enthalpy equation, were used to simply the Gibbs free energy equation to terms of A and PV. This is primary equation ended in terms of A/NkT and the compressibility factor equation:

$$Z = \frac{PV}{NkT}$$

This equation relates a system's known and controlled pressure, volume, and temperature to the system being studied, in this project the aqueous nonionic surfactant system with varied mole fractions of surfactant to water. This change of terms in the Gibbs free energy equation was to maintain the simplicity of the equation of state, which only requires the parameters shown in the compressibility equation.

A second set of equations were then examined as ideal gas state standards to place in our overall equation of state. The same process of starting from one equation and changing the terms was done with the Helmholtz free energy equation

$$A^{ig} = U^{ig} - TS^{ig}$$

as the starting equation, using the definitions of U and S. The T was considered a constant, as the temperature in this equation experiences no change. The equation is Helmholtz free energy in terms of mole fractions of surfactant to water and A^{ig}/NkT for x_1 and x_2, as done with the first set of equations.

The third set of equations were a compilation of the previous two sets into a singular general equation. Up to and including this step, the equations were all kept in the general and did not account for any particular surfactant system. To address the need for a general fit to all possible surfactant systems available. After the combination of the ideal gas state Helmholtz energy equation and the general surfactant/water system Helmholtz energy equation was formed

$$\frac{A^{ig}}{NkT} = \frac{A}{NkT} - \int_0^\eta \frac{Z-1}{\eta} d\eta$$

The equation shown above is the singular ideal gas state form, with the surfactant and water concentration not accounted for. Two nearly identical equations were formed when the concentrations of the system were considered. These three equations were used in a fourth compilation, that converted the previous equations to terms of Z-1/η where

$$Z - 1 = \frac{\theta_1 \eta + \theta_2 \eta^2 + \theta_3 \eta^3}{1 - \beta \eta}$$

and this equation, that accounted for the ideal and actual concentrations of the surfactant/water system was evaluated for their integral terms to yield a ΔG_{mix}/NkT equation that could finally be adjusted for association and related terms.

In the process of evaluating the expression an alternative derivation for ΔG_{mix}/NkT was found. This resulted in a second evaluation of the project up to that point. The sets of equations were refit to attempt to falsify the original derivation. This second derivation was quickly eliminated after this second evaluation as it was figured to be an error in algebra.

The ΔG_{mix}/NkT equation, once solved for the compressibility factor, required a stiffness estimation as this was to be accounted for in calculations. This was needed in order to account for a recent assumptions made that cylindrical micelles actually behave as wormlike spherocylinders as seen in Figure 2. The thermodynamic properties of which can be determined by interpolating between the properties of freely jointed tangent hard-sphere chains and rigid spherocylinders.
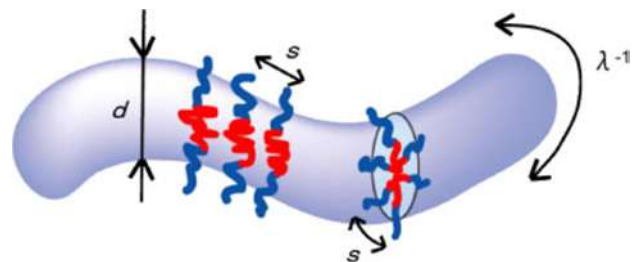

Figure 2: Wormlike micelle

A window of parameters was investigated for each variable input in the equations. Eta, η, stiffness, s, and chain length, m, were given approximate minimum and maximum values during the initial development of the association term.

$$\eta = (\eta)_m = (\eta)_w$$

This eta equality assumes volume additivity for all micelle-water mixtures and was given a range from 0.05 to 0.50 in concentration. The minimum of 0.05 was used to keep

calculations in a range of values that were probable and useable to as many surfactant/water systems as possible.

The stiffness factor, s, was given a range of 0 to 1.0 to include a completely wormlike behavior, a completely rigid spherocylinder, and the varying degrees of the two absolutes.

$$(m)_m = (\gamma)_m$$

Micelle chain length had a rather large range from 10 to 1000 to fit the range of simple fluids and complex fluids in the surfactant/water system.

This equation of state was expressed in terms of a reduced Helmholtz free energy expansion

$$\frac{A}{NkT} = \frac{A_{ig}}{NkT} + \frac{A_{rep}}{NkT} + \frac{A_{dis}}{NkT} + \frac{A_{asso}}{NkT}$$

where the subscripts rep, dis and asso stand for repulsion, dispersion and association respectively. The variable N is the total number of molecules in the system. This equation was differentiated according to the thermodynamic relation

$$Z = \eta \left[\frac{\partial \left(\frac{A}{NkT} \right)}{\partial \eta} \right]_{T,P}$$

To give an expression for the compressibility factor of the surfactant micelle-water mixture

$$Z = 1 + Z_{rep} + Z_{dis} + Z_{asso}$$

Data for hard-sphere chains were fit up to 201 tangent segments, m, to a simple EOS in packing fraction

$$Z = 1 + \frac{\theta_1 \eta + \theta_2 \eta^2 + \theta_3 \eta^3}{1 - \beta \eta}$$

with the parameters given by

$$\theta_{1-hsc} = 2.547 + 0.9242(m-1)$$
$$\theta_{2-hsc} = 5.3696 + 7.8864(m-1)$$
$$\theta_{3-hsc} = 0$$

And the variable beta, β=1.453. These equations contain the correct limit when compared to the simulation data for the hard-sphere fluid when chain length, m=1 and apply also to the solvent water.

Then Z versus η data was generated for hard-spherocylinders of various lengths, up to limits provided by the available data, using a previous Nezbeda equation of state for pure hard-spherocylinders

$$Z = \frac{1 + (3\alpha - 2)\eta + (\alpha^2 + \alpha - 1)\eta^2 - (5\alpha^2 - 4\alpha)\eta^3}{(1-\eta)^3}$$

where the non-sphericity parameter α is given by the relation

$$\alpha = \frac{\gamma(\gamma+1)}{3\gamma - 1}$$

With the subsequent relation of gamma, γ, as seen below

$$\gamma = \frac{\sigma + L}{\sigma}$$

The data generated from the hard sphere chains were also accurately refit with the parameters as follows

$$\theta_{1-cyl} = 2.547 + 0.8395(\gamma-1) - 0.0335(\gamma-1)^2$$
$$\theta_{2-cyl} = 5.3696 + 3.9554(\gamma-1) + 0.4987(\gamma-1)^2$$
$$\theta_{3-cyl} = \qquad -1.4211(\gamma-1) - 1.5866(\gamma-1)^2$$

A final observation made was that for γ(m)=1 the final equation reduces to the equation of state for hard-spheres.

Cylindrical, rodlike, micelles were anticipated to be flexible wormlike spherocylinders, so that the true compressibility factor versus packing fraction for these micelles would be somewhere between the flexible hard-sphere chain compressibility factor and the rigid hard-spherocylinder compressibility factor. This is where the stiffness parameter was used again. A presumed linear interpolation between the two extreme cases so that the parameters in the earlier equations came out to be:

$$\theta_{1m} = s\theta_{1-cyl} + (1-s)\theta_{1-hsc}$$
$$\theta_{2m} = s\theta_{2-cyl} + (1-s)\theta_{2-hsc}$$
$$\theta_{3m} = s\theta_{3-cyl}$$

which were a compilation of the theta cylinder and theta hard sphere chain equations.

$$\frac{\Delta G_{mix}}{RT} = Z - x_m Z_m - x_w Z_w - \ln Z + x_m \ln Z_m + x_w \ln Z_w + x_m \ln x_m + x_w \ln x_w$$
$$+ \int_0^\eta \frac{Z-1}{\eta} d\eta - x_m \int_0^{\eta_m} \frac{Z_m - 1}{\eta_m} d\eta_m - x_w \int_0^{\eta_w} \frac{Z_w - 1}{\eta_w} d\eta_w$$

Solution of the total equation shown above requires equations of state $Z = Z(h)$, $Z_m = Z_m(\eta_m)$ and $Z_w = Z_w(\eta_w)$ to develop the required molecular contributions to the compressibility factors, and arrive at an accurate equation of state for these systems that can be used to predict multiple liquid phase behavior of aqueous nonionic surfactant systems. This was the completion of the project thus far- a

macroscopic model of a system of wormlike micelles and water.

Upon completion of the general macroscopic model and its approximate limits, the microscopic molecular thermodynamic model of micellization had to be addressed. This was divided into negative and positive Gibbs free energy contributions.

The negative Gibbs free energy contribution, $g_{w/hc}$, was expressed in terms of enthalpic and entropic contributions:

$$g_{w/hc} = h_{w/hc} - T s_{w/hc}$$

The second effect is the formation of a planar, or curved, hydrocarbon-water interface for disk like, cylindrical, or spherical micelles that is corrected for head group screening.

The positive Gibbs free energy of interface formation is given by:

$$g_\sigma = \sigma(a - a_0)$$

where σ is interfacial tension, energy divided by area, and the interfacial area per monomer, a, is

$$a = \frac{Sv}{l_c}$$

In this equation S is the shape factor, numbers 1 through 3 for disks, cylinders or spheres respectively and l_c is the micelle core minor radius. Continuing with the Gibbs free energy of interface formation, a_0 represents the average area of the interface per monomer screened by the head group which is a fixed value of a_0=21 A^2, Angstroms squared.

The volume of the hydrocarbon tail, v, is given by

$$v = 27.4 - 26.9(n_C - 1)$$

where v is in A^3 and n_c is the tail portion of the surfactant's chain length. The final portion of the Gibbs free energy equation is the steric contribution to the Gibbs free energy of micellization, g_{st}, and it is expressed as an ideal-localized monolayer as

$$g_{st} = -kT \ln\left(1 - \frac{a_h}{a}\right)$$

where a_h is the head group average cross-sectional area in A^2

$$a_h(j,T) = 38.1[1 - 0.0075(T - 298.15)]\left(\frac{j}{6}\right)^{0.8}$$

where j is the number of ethylene oxide, CH_2CH_2-0-, head group units.

Finally the Gibbs free energy of micellization, G_{mic} in terms of kT, is determined from the sum of the four contribution discussed above as shown below

$$g_{mic} = g_{w/hc} + g_\sigma + g_{hc/mic} + g_{st}$$

The system of equations used to yield this final equation gives g_{mic} as a function of micelle shape S and core radius l_c in terms of Angstroms. Determination of the optimum shape and size micelle was done so by varying l_c for each of the three S shapes to obtain the value of l_c for which the minimum in g_{mic} is observed. This was considered the optimum value l_c* for that shape. The optimum shape S* is the shape for which the absolute minimum g_{mic}* of the three shapes was achieved.

This procedure, when completed generally, yielded infinitely long cylindrical micelles as the optimum aggregate. To address this issue, experimental data was used and gave evidence that indicated that a distribution of sizes of cylindrical micelles would actually be observed. Here, the free energy of a rod like micelle of aggregation number n is obtained by the interpolation between the free energies of an infinitely long, optimum cylindrical micelle and an optimum size spherical micelle as seen below

$$g_{mic}(n) = g_{mic}^*(cyl) + \left(\frac{n_{sph}^*}{n}\right)\left[g_{mic}^*(sph) - g_{mic}^*(cyl)\right]$$

with the optimum size of a spherical micelle was given by

$$n_{sph}^* = \frac{4\pi d_c^*}{3v}$$

Here the variables were all previously calculated in various equations within the primary Gibbs free energy equation used.
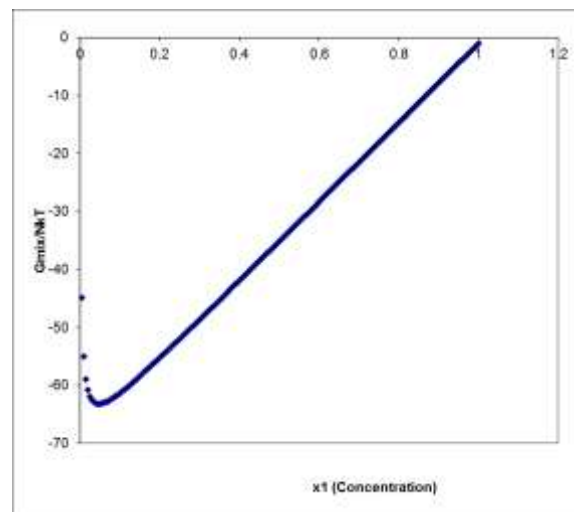

Figure 3: Graph of concentration versus resulting Gibbs free energy calculation

Figure 3 is a visual representation of the G_{mic} equation at concentrations of surfactant from 0, where there is no surfactant in the system, to 1 where there is a theoretical one hundred percent concentration of surfactant in the system.

Discussion/Conclusion

This model required a vast foundation of thermodynamics and chemical engineering foundation. The largest issue in this project was the necessity to learn and understand these concepts prior to the next step in the development process. The project itself was an experience in self-teaching and in self-guided research. Although the concept for this project appeared clear cut, the process was delayed multiple times to accommodate discoveries and unexpected errors that were found in the reevaluation process.

The project aimed to combine the simplicity of a cubic equation of state and the descriptive properties of the free energy equation. The G_{mic}-SAFT equation of state that was developed in this project does just that. With respect to very basic data that can be found for the systems one is studying, this interworking equation can accurately estimate many facets of a surfactant/water system's thermophysical properties. The limits of stiffness and chain length were not explicitly defined in this work. Some approximate limits were used in this project to develop the general equation and will be explored in greater detail in later work.

References

Gow, A. S. and M. J. Macias, *A Hybrid Free Energy of Micellization Model - SAFT-Type Equation of State for Aqueous Nonionic Surfactant Systems*, SAFT 2015, Houston, TX, May 2015.

Gow A. S., M. J. Macias and J. Liu. *gmic-SAFT: A Hybrid Free Energy of Micellization / Equation of State Model for Aqueous Nonionic Surfactant Systems*, Fluid Phase Equilibria., Manuscript in Review.

Gow, A. S. and R. B. Kelly, *Twenty-One New Theoretically Based Cubic Equations of State for Athermal Hard-Sphere Chain Pure Fluids and Mixtures*, AIChE J.

Puvvada, S. and D. Blankschtein, *Molecular-Thermodynamic Approach to Predict Micellization, Phase Behavior and Phase Separation of Micellar Solutions. I. Application to Nonionic Surfactants*, J. Chem. Phys., **92**, 3710-3724 (1990).

Biography

Manette Jazel Macias, originally from Minneapolis, Minnesota, calls Garden Grove, California her home. Manette is a current senior who will be graduating in May 2016 with a B.S. degree in both Chemistry and Forensic Science. She is a member of the Undergraduate Chapter of American Chemical Society on campus and is currently working part-time at a research laboratory with a desire to continue her work there after graduation. Manette plans on furthering her education in graduate school in higher level Chemistry.