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

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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 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, 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 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:

$$g_{w/hc} \quad h_{w/hc} \quad Ts_{w/hc}$$

The second effect is the formation of a planar, or curved, hydrocarbon-water interface for disk like, cylindrical, or spherical micelles that is corr

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.

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