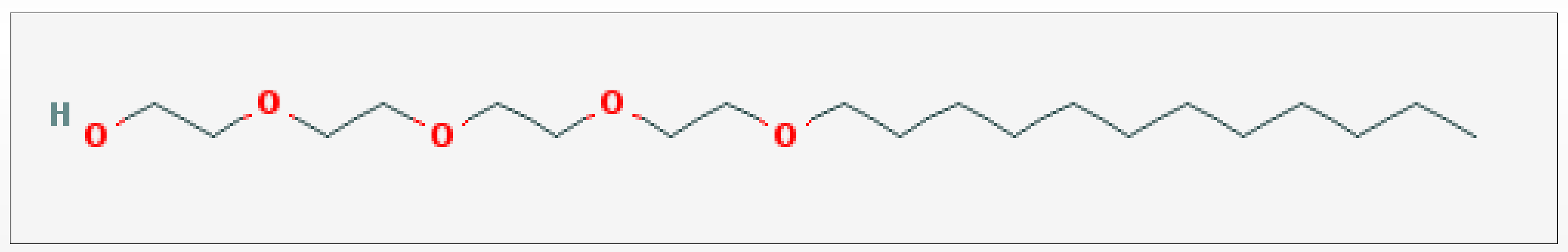
G_{mic}-SAFT: A Hybrid Free Energy of Micellization / Equation of State Model for Aqueous Nonionic Surfactant Systems

Manette Macias **Advisor: Dr. Art Gow**

Introduction

The interest in this project is the development of an equation of state (EOS) for nonionic surfactants in water, that works with the Gibbs free energy equation. The equation enables rapid and accurate screening of micelles by their physical and thermophysical properties. The equation was developed using the polyoxyethylene glycol monoether family (pictured below) because its variable chain length.



Methodology

Refit data for athermal hard spherocylinders from previous work by Nezbeda

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

$$\alpha = \frac{\gamma(\gamma+1)}{3\gamma-1} \qquad \gamma = \frac{\sigma+L}{\sigma} = m \text{ (for chains)}$$

To a slightly modified form of vdWS2-1 EOS

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

$$\beta = 1.453 \qquad \theta_1 = 2.547+0.8395(m-1)\text{-}0.0335(m-1)^2$$

$$\theta_2 = 5.3696+3.9554(m-1)+0.4987(m-1)^2$$

$$\theta_3 = -1.4211(m-1)-1.5866(m-1)^2$$

Pair the G_{mic} Equation with EOS

Results

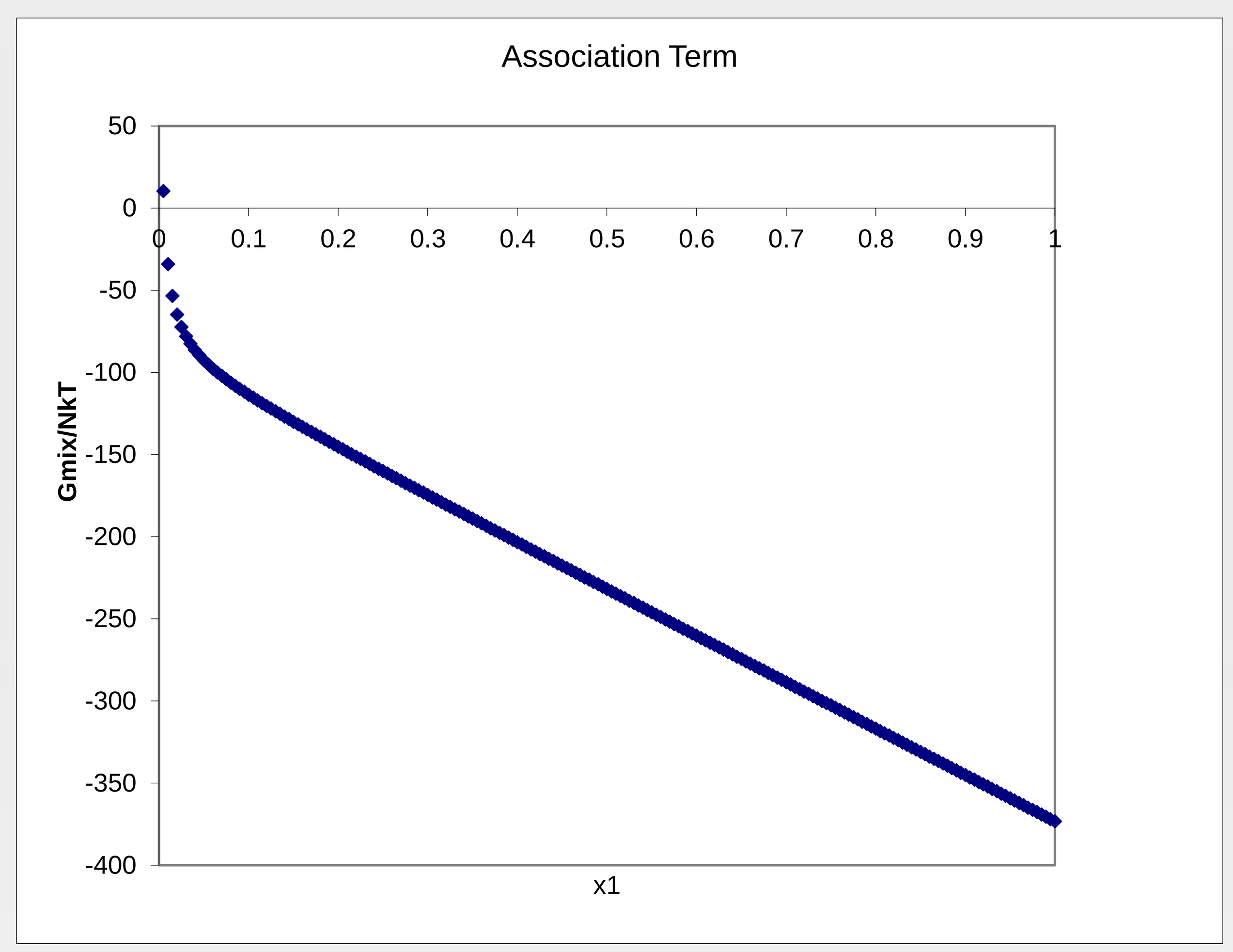
These theta equations are the backbone to the association term of this hybrid equation. It accounts for a blend of cylindrical shape and hard sphere chains, along with the effects of water.

The last four equations are the micelle and water calculations prior to adding the forces together- the last step in the hybrid equation.

gamma	201
K	0.1
stiffness	0.1
theta1-hsc	187.387
theta2-hsc	1582.65
theta1-cyl	-1169.55
theta2-cyl	20744.45
theta3-cyl	-63748.2
theta1-H2C	2.547
theta2-H2C	5.3696
theta1-mic	51.693
theta2-mic	3498.83
theta3-mic	-6374.82
eta	0.5
Gmic	-80.8136
GH2O	3.722193
Zmic	379.1633
ZH2O	9.564534

K and β are the only constants used in these series of equations.

These four equations respond to the changes in the theta equations, generated from user defined gamma, stiffness, and eta parameters.



Conclusions

This project aimed to combine the simplicity of a cubic equation of state and the descriptive properties of the free energy equation. G_{mic}-SAFT does that, with respect to user defined limits of stiffness and chain length- the limits of which are to be further defined in later work.

This model gives accurate estimates of:

- critical micelle concentration (CMC)
- optimum shape and size micelle
- micellar size distribution
- weight average micellar aggregation number

This hybrid can be used to rapidly screen surfactant solutions for the existence two-aqueous phase micellar systems to quickly find the most attractive ones for new separation processes.

Acknowledgements

Carol Withers, Erica Dafilis, and Janice Sanderson for their patience and assistance throughout the 2015 SURF Program

Mr. and Mrs. Carruba and everyone else involved in the SURF Program

Dr. Art Gow for his role as project advisor

References

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).

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