Robust Flash Calculation Algorithm for Microemulsion Phase Behavior

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Introduction

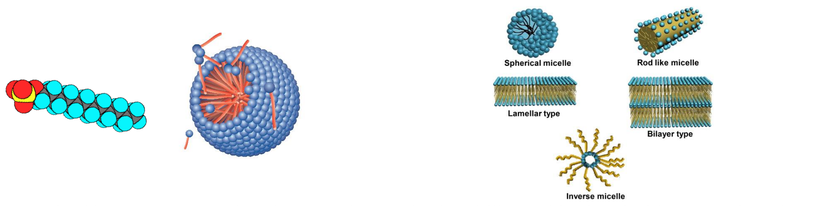


Figure 1: (Left) Surfactant molecules consists of hydrophilic and hydrophobic parts therefore the molecules form aggregates. (Right) The molecules aggregate in different structures. Surfactants can create a homogenous mixture of oleic and aqueous components. [1]

Surfactant can dissolve oleic and aqueous phases to form microemulsions (Figure 1). Therefore they are used widely in different industries for emulsification, homogenization and separation (Figure 2).

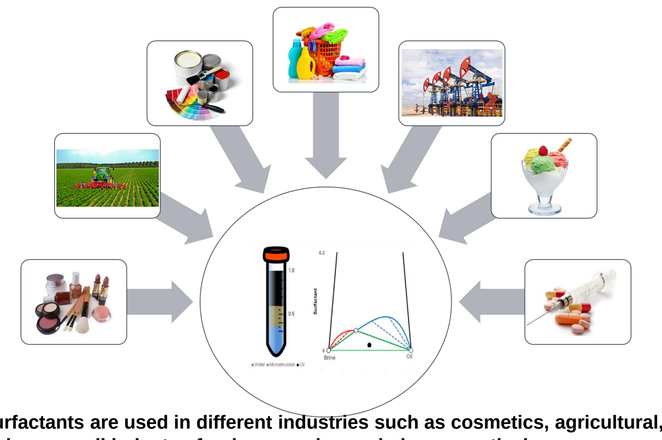


Figure 2: Surfactants are used in different industries such as cosmetics, agricultural, paints, household cleaners, oil industry, food processing and pharmaceutical.

Problem Definition

The current state-of-the art for microemulsion phase behavior prediction has the following problems:

1. Current models for microemulsion phase behavior fit experimental data. These models, however, cannot predict phase behavior (phase amounts and compositions) for changing formulation variables, such as temperature, pressure, overall composition, surfactant molecular properties. Such predictions are important for many applications that currently rely solely on experimentation.
2. Modern and physical based phase behavior models such as HLD-NAC (hydrophylic-lipophylic and net-average curvature) are not consistent over the entire range of formulation variables, and thus could not be used in simulation or for more general design and predictive uses.

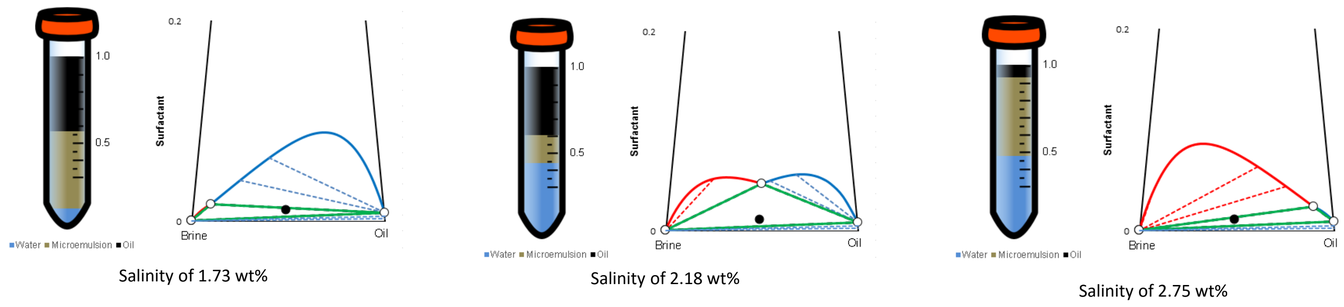


Figure 3: Microemulsion phase behavior is affected by many parameters such as salinity. Therefore different amount of phases will form for the same amount of surfactant.

Modeling

Our flash algorithm uses the HLD-NAC[2] model to calculate microemulsion phase behavior. The surfactant affinity is quantified by HLD. Micelle sizes and distribution are estimated by NAC as a function of HLD.

Surfactant affinity: The difference between surfactant affinity to aqueous and oleic components is the key parameter which determines microemulsion phase behavior. The following is the most important models for surfactant affinity.

Hydrophilic Lipophilic balance (HLB) (Griffin 1949):

- Only considers surfactant properties.

R-ratio (Winsor 1954):

- Difficult to measure

Hydrophilic Lipophilic Difference (HLD) (Salager *et al.* 1979, 1988, 2000)

- Correlated to oil, water, and surfactant properties

$$\mathcal{H} = \ln\left(\frac{S}{S_r}\right) - K(EACN - EACN_r) - \alpha(T - T_r) - \beta(P - P_r) - \mathcal{H}_r$$

where $\mathcal{H}$ is HLD, $\boldsymbol{S}$ is effective salinity, $\boldsymbol{EACN}$ is equivalent alkane carbon number, $\boldsymbol{T}$ is temperature, $\boldsymbol{P}$ is pressure, subscript $\boldsymbol{r}$ stands for reference point.

Curvatures: Acosta et al. (2003) correlated micelle curvature to Gibbs energy of formation of micelles. They correlated net curvature to HLD. In addition, the results of De Gennes and Tupin (1982) bound the micelle curvature.

Net curvature relationship to HLD

$$\left(\left|\frac{1}{R_o}\right| - \left|\frac{1}{R_w}\right|\right) = -\frac{\mathcal{H}}{L}$$

Micelle sizes are bounded

$$\frac{1}{2}\left(\left|\frac{1}{R_o}\right| + \left|\frac{1}{R_w}\right|\right) \geq \frac{1}{\xi}$$

Definitions:

$$I = V_s/A_s L \qquad \text{Ghosh and Johns (2016)} \qquad \xi_D = \xi/L$$

$$\sigma_i = V_i/V_s\ , \qquad i = o, w$$

$$R_i = 3(V_i + 0.5V_s)/A_s \implies R_i = 3IL(\sigma_i + 0.5)$$

We extended the NAC model to the two-phase region by parametrizing tie lines. The values of ξ are calculated by interpolating between the critical tie-line and tie-triangle (Figure 5).

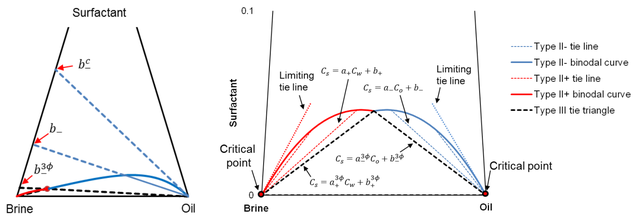


Figure 4: Tie line parametrization for type II- region (left) and for all three regions (right).

The algorithm in Figure 5 is used to calculate phase saturations and compositions.

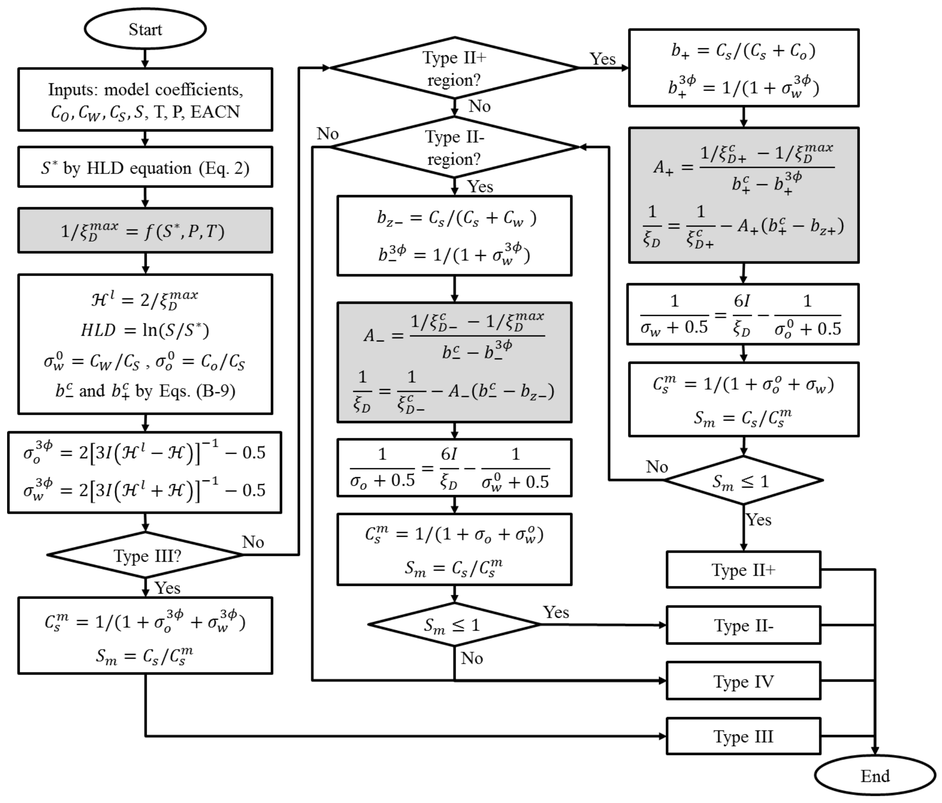
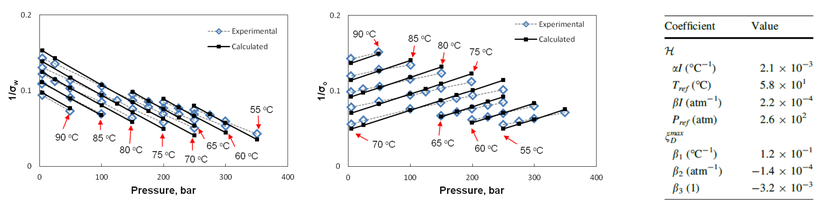


Figure 5: Detailed flow chart for new flash calculation algorithm. The gray blocks represent the equations added in this research to complete the model. If data is available, these equations can be further improved, but for our purposes we have selected the simplest possible models.

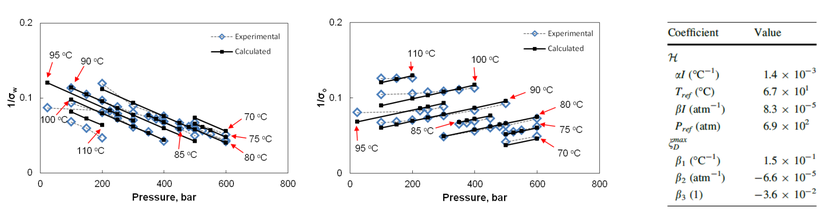
Results

The accuracy and consistency of the algorithm was tested by tuning the model with several sets of published microemulsion phase behavior data.



Coefficient	Value
$\mathcal{H}$	
αI (°C^{-1})	2.1×10^{-3}
T_{ref} (°C)	5.8×10^{1}
βI (atm^{-1})	2.2×10^{-4}
P_{ref} (atm)	2.6×10^{2}
$\frac{1}{\xi_D^{max}}$	
β_1 (°C^{-1})	1.2×10^{-1}
β_2 (atm^{-1})	-1.4×10^{-4}
β_3 (1)	-3.2×10^{-3}

Figure 6: Comparison of predicted and fitted data of Austad and Strand (1996) using their dead oil experiments. Only experimental data at 65 and 80 ˚C was used for tuning. The experimental data at 55, 60, 70, 75, 85, and 90 ˚C are predicted.



Coefficient	Value
$\mathcal{H}$	
αI (°C^{-1})	1.4×10^{-3}
T_{ref} (°C)	6.7×10^{1}
βI (atm^{-1})	8.3×10^{-5}
P_{ref} (atm)	6.9×10^{2}
$\frac{1}{\xi_D^{max}}$	
β_1 (°C^{-1})	1.5×10^{-1}
β_2 (atm^{-1})	-6.6×10^{-5}
β_3 (1)	-3.6×10^{-2}

Figure 7: Comparison of predicted and fitted data for the live oil experiments from Austad and Strand (1996). Only experimental data at 80 and 100 ˚C are used for tuning. The experimental data at 70, 75, 85, 90, 95, and 110 ˚C are predicted.

We modified the micelle radius equation by adding half of the surfactant volume into the micelle radius. The new model allows for tie lines along the side of the phase diagram where oil or water components are not present.

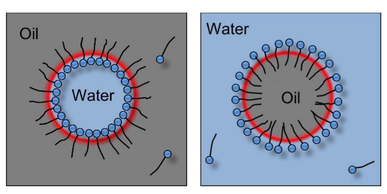


Figure 8: The red line shows the hypothetical interface that encompasses some surfactant volume. Surfactant volume is generally negligible, but becomes more important as the size of micelles decrease near the phase diagram boundaries.

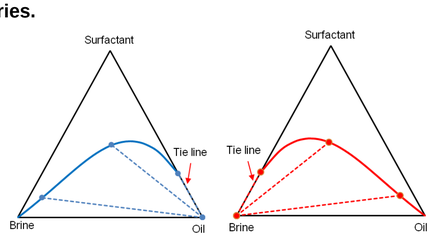


Figure 9: The critical tie-line is no longer present inside the ternary diagram at large deviation from optimum conditions. HLD is -1.7 for the left figure and 1.7 in the right figure based on the tuning of data from Roshanfekr and Johns (2011).

Conclusions

We presented the first flash calculation algorithm based on HLD-NAC that can model all Winsor regions. The model assumes pure excess phases. A detailed flow chart for the algorithm is given, and the results of tuning and prediction were demonstrated for several fluids. Key conclusions are:

- The dimensionless characteristic length is calculated as a function of HLD and overall composition for the two-phase regions. A new empirical relation is given for correlation length in the two-phase regions that is based on an exponential trend with HLD, but linear interpolation within the two-phase regions at constant HLD.
- Immiscibility between surfactant and oil or water is modeled in the new algorithm by accounting for surfactant volume in small micelles.
- New correlations for solubilization ratio of optimum formulation are developed that allow for variations in any formulation parameter(s). The correlations gave good predictions of solubilization ratios at optimum formulation. In this model, the characteristic length is assumed constant in the three-phase region.
- The flash is non-iterative and completely robust. Phase labeling and identification are not issues because the limiting tie line at the critical point is calculated directly.

Footnotes

1- Figures sources: (left) ilpi.com, (middle) dataphysics.de, (right) Pal & Bhaumik (2013) Adv. Colloid Interface Sci.

1- Hydrophilic-Lipophilic Difference – Net and Average Curvature

PennSurf online app for the algorithm

Khorsandi and Johns (2016)