Curvature-Based Equation-of-State for Microemulsion Phase Behavior

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Abstract

An accurate description of microemulsion phase behavior is critical for many industrial applications, including surfactant flooding in enhanced oil recovery. Recent phase behavior models have assumed constant-shaped micelles, typically spherical, using net average curvature (NAC), which is not consistent with scattering and microscopy experiments that suggest changes in shapes of the continuous and discontinuous domains. Based on the strong evidence of varying micellar shape, principle micellar curves were recently used to model interfacial tensions (IFT). Huh's scaling equation was also coupled to this IFT model to generate phase behavior estimates, but without accounting for micellar shape.

In this paper, we present a novel microemulsion phase behavior equation-of-state (EoS) that accounts for changing micellar curvatures under the assumption of a general prolate spheroidal geometry, instead of through Huh's equation. This new EoS improves phase behavior modeling capabilities and eliminates the use of NAC in favor of a more physical definition of characteristic length. Our new EoS can be used to fit and predict microemulsion phase behavior irrespective of IFT data availability. For the cases considered, the new EoS agrees well with experimental data for scans in both salinity and composition. The model also predicts phase behavior data for a wide range of temperature and pressure, and is validated against dynamic scattering experiments, to show the physical significance of the approach.

1. Introduction

The interaction of surfactant, oil and brine components can result in the formation of a microemulsion, which is an isotropic, macroscopically homogeneous, and thermodynamically stable phase (Strey, 1993). Microscopically, the surfactant forms an interfacial layer separating the oil and brine domains, which are around 100-1000 Å in size (Chandra and Safran, 1991). In these systems, the formulation variables can be modified to yield structures where the interfacial layer preferentially bends towards the oil or brine (Chandra and Safran, 1991). Microemulsion systems are of special interest for tertiary recovery applications, given the system's ability to yield ultra-low interfacial tensions (less than 10^{-3} mN/m) between the relevant phases. Ultra-low IFT mobilizes oil previously trapped by capillary forces (Healy and Reed, 1974).

1.1. Surfactant affinity

During a typical formulation variable scan, different microemulsion environments exist that are denoted by the number of phases present and the composition of the microemulsion phase. For a hydrophilic state, the system generally exhibits only two coexisting phases: a brine-continuous microemulsion with oil-internal micelles in equilibrium with an excess oil phase. This environment is known as type II- or Winsor I. For a lipophilic state, the system generally exhibits two coexisting phases: an oil-continuous microemulsion with brine-internal micelles in equilibrium with an excess brine phase. This environment is known as type II+ or Winsor II. Finally, for a balanced

affinity state, the system exhibits three coexisting phases: a microemulsion phase in equilibrium with excess brine and oil phases. This environment is referred to as type III or Winsor III (Davis, 1994).

Surfactant affinity to either component can be quantified through a variety of measures, including the hydrophilic-lipophilic balance (HLB), the phase inversion temperature (PIT) or the R-ratio (Davis, 1994). Salager et al. (2000) introduced the hydrophilic-lipophilic difference (HLD, denoted as $\mathcal{H}$ in this paper), as a measure of surfactant affinity that can be directly tied to surfactant partitioning between the oil and brine phases. The state function $\mathcal{H}$ captures the effect of multiple formulation variables changing simultaneously (Marquez et al., 2002; Ghosh and Johns, 2016; Khorsandi and Johns, 2016; Torrealba and Johns, 2017B).

1.2. Correlation length

The quality of a microemulsion system can be assessed by the capacity to solubilize oil and brine components for a given surfactant concentration. Better quality means greater solubilization and lower IFT, which implies that the three-phase invariant point (microemulsion phase composition) is nearer to the oil-brine axis of the ternary diagram (Torrealba and Johns, 2018). Quality is therefore directly related to the correlation length of the microemulsion phase (ξ), which can be defined as the inverse of total interfacial surface area over unit volume of the microemulsion phase (S/V) (Debye et al., 1957; Talmon and Prager, 1978; De Gennes and Taupin, 1982; Peltomäki et al., 2012). From this definition, $\xi = r/3$ for spherical micelles of radius r when surfactant volume is neglected.

Oil-internal micelles have positive curvature, while brine-internal micelles negative curvature. Strey (1994) proposed that the mean curvature (C_m) of all oil and brine micelles present in the type III region should change with temperature as shown in Fig. 1 (represented here by $\mathcal{H}$). The characteristic radii approach each other at the extreme limits in $\mathcal{H}$ so that micelles are spherical there. In the type III environment, micelles resemble a bicontinuous microstructure. At optimum, there is equal number of oil and brine micelles of similar volumes so that the average mean curvature becomes zero.

For tertiary oil recovery, the microemulsion phase behavior is often designed to transition between the type II- environment (corresponding to $C_m > 0$) and type II+ environment (corresponding to $C_m < 0$) to ensure the optimum in the Winsor III region is crossed. At optimum, the average mean curvature vanishes in the bicontinuous regime and oil-brine interfacial tension is the smallest. The correlation length ξ , if defined as the inverse of C_m , becomes infinite at optimum. Strey (1994; 1996) therefore proposed an empirical definition of the correlation length that is finite and consistent across all phase environments based on the principal curvatures of the micelles. The correlation length of a microemulsion with a set of oil and brine micelles can be expressed by,

$$\xi = \sqrt{\frac{2}{c_1^2 + c_2^2}} , \quad (1)$$

where c_1 is the average curvature of the brine micelles, and c_2 is the average curvature of the oil micelles in the three-phase region. This definition of correlation length is equal to r for spherical micelles, which is consistent with the S/V correlation length definition.

The correlation length of microemulsions defined by Eqn. 1 has been compared to experimentally determined values as a function of relevant formulation variables. Strey (1994) studied the correlation length for an oil-water- $C_{12}E_5$ system as a function of temperature. Sottmann et al. (1997) presented the correlation length for an oil-water- C_jE_k system as a function of the carbon number of the alkyl chain (j) and the surfactant head group size (k). Berghaus et al. (2016) estimated the correlation length for an oil-water- $C_{10}E_4$ system as a function of pressure. The correlation length is observed to have a similar behavior for changes in different formulation variables. This motivated the scaling of the correlation length with $\mathcal{H}$, as shown by Torrealba and Johns (2017A).

For phase behavior estimation in this paper, we use the definition of correlation length based on the ratio of the volume to the surface area of micelles, which is consistent with the definition of previous models (Debye et al., 1957; Talmon and Prager, 1978; De Gennes and Taupin, 1982). This definition for correlation length allows for various micellar shapes, is more physical than that defined in Eqn. 1, and can be easily connected to microemulsion solubilized volumes.

1.3. State-of-the-Art in HLD-NAC models

Acosta et al. (2003) introduced a microemulsion phase behavior model based on net and average curvatures (NAC). The average curvature in the HLD-NAC model is defined as the average of the oil and brine curvatures, where micelles are assumed to always be the same shape, typically spherical, even in the Winsor III region. The net curvature is defined as the difference between the oil and brine curvatures. With these two equations the model allows for an estimation of oil and brine solubilization ratios for different $\mathcal{H}$ values, but is unphysical as it assumes both oil and brine spherical micelles exist across all microemulsion environments. This definition of the correlation length is not consistent with Eqn. 1 or S/V . For example, in a type II- environment, the model assumes the continuous brine component can be approximated by spherical micelles, even though brine is the continuous phase in that region. Kiran and Acosta (2010) proposed a variation to the original NAC equations to consider cylindrical micelles with spherical end caps, which allowed them to better capture microemulsion viscosity near phase transitions. However, their model did not produce continuous transitions from type II- to type II+.

HLD-NAC has been successfully used to model the phase behavior of oil-brine-surfactant systems for a wide variety of cases (Acosta, 2008; Acosta et al., 2012; Kiran and Acosta, 2015; Ghosh and Johns, 2016; Jin et al., 2017). Khorsandi and Johns (2016; 2017) noted the original HLD-NAC equations yielded unphysical results in both type II- and type II+ environments and developed the first equation-of-state (EoS) to compute physical and consistent predictions of phase amounts and compositions for all Winsor regions by modeling the correlation length at the critical points in the two-phase lobes. They defined a dimensionless correlation length based on the average curvature definition of Acosta et al. (2003) corrected to include surfactant volume in the spherical micelles and also introduced a correlation for optimum conditions that made HLD-NAC predictive. Khorsandi and Johns, however, did not account for nonspherical micellar shapes.

1.4. Interfacial tension

Huh (1979; 1983) presented a scaling between oil and brine solubilization ratios and the relevant interfacial tensions using,

$$\begin{aligned}\gamma_{om} &= \frac{\Omega}{\sigma_o^2} \\ \gamma_{mw} &= \frac{\Omega}{\sigma_w^2},\end{aligned}\tag{2}$$

where Ω is a scaling constant (usually near 0.3 mN/m), σ_i is the solubilization ratio of component i defined by $\sigma_i \equiv C_{im}/C_{sm}$ with C_{im} equal to the concentration of component i in the microemulsion phase, and γ_{jk} is the interfacial tension between phases j and k . Huh assumed the microemulsion phase to be alternating layers of oil and brine (i.e. bicontinuity), making Eqn. 2 geometrically representative only in the three-phase region.

Torrealba and Johns (2017A) presented an interfacial tension model that allows for a complete description of microemulsion systems for any overall composition and set of formulation variables (e.g. pressure, temperature, salinity, etc.). Interfacial tensions are defined using principal curvatures and phase transition boundary conditions. Their model combined with Huh's equation allows for the accurate prediction of phase behavior based on tuned interfacial tension data. They showed that a combination of the type III oil-microemulsion and microemulsion-brine model interfacial tensions using Huh's equation (Huh, 1979; Huh, 1983) resulted in expressions for the type III oil and brine solubilization as,

$$\begin{aligned}\sigma_o^{III} &= \sigma^* \left(\frac{\mathcal{H}_U}{\mathcal{H}_U - \mathcal{H}} \right) \\ \sigma_w^{III} &= \sigma^* \left(\frac{\mathcal{H}_L}{\mathcal{H}_L - \mathcal{H}} \right),\end{aligned}\tag{3}$$

where σ^* is the optimum solubilization ratio, and $\mathcal{H}_L$ and $\mathcal{H}_U$ are the $\mathcal{H}$ limits where the invariant point (i.e., the type III microemulsion composition) coincides with the type II+ and type II- critical points, respectively. Under the assumption of pure excess phases, the type II+ critical point is located at the pure brine apex, and the type II- critical point is located at the pure oil apex. Although the model by Torrealba and Johns (2017A) uses principal curvatures to compute interfacial tensions rigorously for practical applications, it did not use principal curvatures to compute phase behavior.

1.5. Origin of micellar shapes

Early theoretical considerations by Tartar (1955) indicated that the interplay of forces during micelle formation in aqueous solutions of ionic surfactants may result in their deviation from spherical geometry. As micelles form, energy is liberated by the removal of a number of hydrocarbon chains from the surrounding brine, thereby decreasing the hydrocarbon-brine interfacial area. In addition, strong cohesive forces between brine molecules aggregate and expel the surfactant chains from solution. These molecular forces are short range (i.e., van der Waals forces). As the surfactant chains are increasingly packed, their electrically charged polar ends are brought closer. Repulsive forces between the surfactant heads are long range electrical forces (i.e., Coulombic forces). The resulting geometry of the micelle is determined by the interplay of these forces. Tanford (1972, 1974) also showed that most common small soluble micelles must be ellipsoidal rather than spherical in shape. He presented a theory where both spherical and ellipsoidal (including both prolate and oblate spheroids) represent all micellar shapes in the

microemulsion phase. In general, due to the polydispersity in micellar aggregation number and surface area available per polar head groups, there should be a distribution of both sizes and shapes within this family. Tanford (1972) also noted that surfactants with two hydrocarbon chains per head group require smaller surface area per hydrocarbon chain, and hence prefer extended bilayers or vesicle geometries, which agrees with experimental observations.

To capture changes in shape and domain continuity, micelles can be approximated as prolate spheroids, which are defined by the distance r_b from its center to its pole along the symmetry axis and the equatorial radius of the spheroid r_a . These characteristic radii are related to the surface curvatures and also the characteristic length. Prolate spheroids are preferred over oblate spheroids because they better approximate cylindrical micelles associated with the increase in bulk viscosity near phase transitions (Kiran and Acosta, 2015). Further, under flow conditions micelles likely deform toward prolate geometries to minimize drag (Hu and Matthys, 1995). Oblate spheroids, however, could better approximate lamellar structures associated with near optimum conditions (Huh, 1979). A possible extension of the model could consider a distribution of both prolate and oblate spheroids to capture both regimes.

1.6. Improved curvature model for phase behavior estimation

In this paper, we present a simple extension to curvature-based microemulsion phase behavior modeling by accounting for changes in micellar shape. This more physical equation-of-state (EoS) model improves upon the previous flash methodology (Torrealba and Johns, 2017A) by calculating oil and brine solubilization ratios directly from principal curvatures by assuming a prolate spheroid micellar geometry. This eliminates the need for the less physical assumption of constant spherical geometry of the NAC approach. Based on principal curvatures in the three-phase region, we define principal curvatures for all microemulsion compositions for both type II- and II+ environments. The resulting equations in the three-phase region (where bicontinuity is assumed) are consistent with Eqn. 3 in Torrealba and Johns (2017A), which was derived using an IFT approach with principal curvatures. This improved curvature approach is shown to accurately capture both phase behavior for experiments with $\mathcal{H}$ and composition scans. Further, it is shown that the model can be easily defined to predict phase behavior when multiple formulation variables are changing. This approach has the potential to capture the physical mechanism behind the double-peak viscosity behavior exhibited by some microemulsion systems as the type III region is approached. Accurate predictions of phase behavior are important for many industry applications, including surfactant is flooding in the petroleum industry. Finally, we test the qualitative behavior of the curvature model against dynamic light scattering to validate its physical significance.

2. Mathematical Description

For simplicity, our model assumes monodispersity and that all surfactant molecules are adsorbed in the micellar interfacial layer (i.e. excess phases are pure). For either type II- or type II+ environment, we consider micelles to be prolate spheroids such as the ones depicted in Figure 2, where $r_b \geq r_a$. As shown at an oil-water ratio of about unity, micelles are spherical at large positive and negative $\mathcal{H}$ and bicontinuous near optimum conditions. The volume of component i solubilized by the micelle is given by,

$$V_{im} = \frac{4\pi}{3} r_{a,i}^2 r_{b,i}. \quad (4)$$

where $i = o$ for type II- and $i = w$ for type II+. Similarly, the surfactant interfacial area ($A_{s,i}$) is,

$$A_{s,i} = 2\pi r_{a,i}^2 \left(1 + \frac{r_{b,i}}{r_{a,i}t} \sin^{-1} t \right), \quad (5)$$

where $t^2 = 1 - r_{a,i}^2/r_{b,i}^2$. From these equations, the S/V definition of the correlation length is,

$$\xi_i \equiv \frac{V_{im}}{A_{s,i}} = \frac{2r_{b,i}}{3 \left(1 + \frac{r_{b,i}}{r_{a,i}t} \sin^{-1} t \right)}. \quad (6)$$

For an effective length of the surfactant molecule (L), the volume of surfactant in the micelle can be approximated by $V_{sm} = A_{s,i}L$. Therefore, introduction of the solubility ratios into the definition of correlation length in Eqn. 6 gives,

$$\begin{aligned} \xi_o &\equiv \frac{V_{om}}{A_{s,o}} = \frac{V_{om}}{V_{sm}} \frac{V_m}{V_m} L = \frac{C_{om}}{C_{sm}} L = \sigma_o L \\ \xi_w &\equiv \frac{V_{wm}}{A_{s,w}} = \frac{V_{wm}}{V_{sm}} \frac{V_m}{V_m} L = \frac{C_{wm}}{C_{sm}} L = \sigma_w L, \end{aligned} \quad (7)$$

where $C_{im} \equiv V_{im}/V_m$. In dimensionless form, Eqn. 7 becomes,

$$\begin{aligned} \xi_{oD} &\equiv \frac{\xi_o}{L} = \sigma_o \\ \xi_{wD} &\equiv \frac{\xi_w}{L} = \sigma_w. \end{aligned} \quad (8)$$

For the type III environment near optimum, microemulsions consist of complex structures where oil and brine are bicontinuous (Scriven, 1976). Here we approximate this condition with repeating cylindrical domains of oil and brine as $r_{b,i} \rightarrow \infty$. For oil domains in the bicontinuous region, the area term in Eqn. 5 reduces to $A_{s,o} = \pi^2 r_{a,o} r_{b,o}$ (see Appendix A for more details). Thus, for the oil domains in a type III microemulsion Eqns. 7 to 8 reduce to,

$$\xi_{oD}^{III} \equiv \sigma_o^{III} = \frac{V_{om}}{A_{s,o}L} = \frac{4\pi}{3} \frac{r_{a,o}^2 r_{b,o}}{\pi^2 r_{a,o} r_{b,o} L} = \frac{4r_{a,o}}{3\pi L}. \quad (9)$$

For the brine domains, the corresponding expression is,

$$\xi_{wD}^{III} \equiv \sigma_w^{III} = \frac{V_{wm}}{A_{s,w}L} = \frac{4\pi}{3} \frac{r_{a,w}^2 r_{b,w}}{\pi^2 r_{a,w} r_{b,w} L} = \frac{4r_{a,w}}{3\pi L}. \quad (10)$$

The principal curvatures corresponding to the invariant point (i.e., three-phase composition) follow the same form and reasoning as in Torrealba and Johns (2017A),

$$\begin{aligned} c_1^{III} &= c_c(\mathcal{H} - \mathcal{H}_L) \\ c_2^{III} &= c_c(\mathcal{H} - \mathcal{H}_U), \end{aligned} \quad (11)$$

where c_c is the slope of the principal curvatures with $\mathcal{H}$. These curvatures can also be inferred from scattering experiments if available (Strey, 1994). The corresponding radii for each domain are calculated by,

$$\begin{aligned} r_{a,w} &= \left| \frac{1}{c_1^{III}} \right| \\ r_{a,o} &= \left| \frac{1}{c_2^{III}} \right|. \end{aligned} \quad (12)$$

The combination of Eqns. 9-12 with $c_c < 0$ gives the following equations for the oil and brine solubilization ratios in the type III region,

$$\begin{aligned} \sigma_o^{III} &= \frac{4}{3\pi L c_c (\mathcal{H} - \mathcal{H}_U)} \\ \sigma_w^{III} &= \frac{4}{3\pi L c_c (\mathcal{H}_L - \mathcal{H})}. \end{aligned} \quad (13)$$

By noting that $\sigma_o^{III} = \sigma_w^{III} = \sigma^*$ at $\mathcal{H} = 0$ and substituting the corresponding coefficients, Eqn. 13 results in Eqn. 3, which emphasizes the consistency of the current approach with that of Torrealba and Johns (2017A). This result is expected because both rely on principal curvatures in three-phase region as defined by Eqn. 11. One key assumption in Eqn. 13 is that the invariant point composition is always bicontinuous (i.e., $r_{b,i} \rightarrow \infty$). However, as the critical points are approached the size of the domains change accordingly to honor the physical limits. For example, as the invariant point approaches the oil apex (i.e., $\mathcal{H} \rightarrow \mathcal{H}_U$) the size of the oil domains increases to infinity, while the size of the water domains decreases to a non-zero minimum value. The relevance of having a non-zero water domain size is that we can capture a limiting tie line as the critical point is approached (Torrealba and Johns, 2017; Khorsandi and Johns, 2016).

For asymmetric phase behavior in the type III region (i.e., $\mathcal{H}_U \neq -\mathcal{H}_L$), we define $Lc_{co} = -4/(3\pi\mathcal{H}_U\sigma^*)$ and $Lc_{cw} = 4/(3\pi c_c\mathcal{H}_L\sigma^*)$. If accurate data on the effective surfactant lengths is available, then c_{co} and c_{cw} can be calculated accordingly. Otherwise, c_c can be assumed to be $-0.002 \text{ \AA}^{-1}$ as determined by Torrealba and Johns (2017A) based on one data set of scattering from Strey (1994).

Further we define c_i^{cp-} and c_i^{cp+} as the i -th principal curvatures corresponding to type II- and type II+ critical points, respectively. Based on the definition of $\mathcal{H}_L$ and $\mathcal{H}_U$,

$$\begin{aligned} c_i^{cp-} &= c_i^{III} \quad \mathcal{H} = \mathcal{H}_U \quad i = 1,2 \\ c_i^{cp+} &= c_i^{III} \quad \mathcal{H} = \mathcal{H}_L \quad i = 1,2. \end{aligned} \quad (14)$$

A zeroth-order approximation is to assume a constant value of the critical point principal curvatures based on Eqn. 14. In this paper, we consider a limiting value for c_i^{cp-} and c_i^{cp+} as $\mathcal{H}$ approaches $-\infty$ and ∞ , respectively, as shown below,

$$\begin{aligned} c_i^{cp-} &= c_{i,\infty}^{cp-} & \mathcal{H} &= -\infty & i &= 1,2 \\ c_i^{cp+} &= c_{i,\infty}^{cp+} & \mathcal{H} &= \infty & i &= 1,2. \end{aligned} \quad (15)$$

For $-\infty < \mathcal{H} \leq \mathcal{H}_U$, c_i^{cp-} is estimated using the following simple interpolation function similar to that suggested by Khorsandi and Johns (2016),

$$c_i^{cp-} = c_{i,\infty}^{cp-} + A_{c_i}^{cp-} b_{H-} \quad i = 1,2, \quad (16)$$

where $b_{H-} = 1/(1 + \mathcal{H}_U - \mathcal{H})$ is the interpolation variable, and $A_{c_i}^{cp-}$ is a constant defined by evaluating Eqn. 16 at $\mathcal{H}_U$ based on Eqn. 14. Similarly, for $\mathcal{H}_L \leq \mathcal{H} < \infty$, we can estimate c_i^{cp+} by,

$$c_i^{cp+} = c_{i,\infty}^{cp+} + A_{c_i}^{cp+} b_{H+} \quad i = 1,2, \quad (17)$$

where $b_{H+} = 1/(1 + \mathcal{H} - \mathcal{H}_L)$ in the interpolation variable, and $A_{c_i}^{cp+}$ is a constant defined by evaluating Eqn. 17 at $\mathcal{H}_L$ based on Eqn. 14. Khorsandi and Johns (2016) used a similar interpolation in composition space for their definition of correlation length, whereas our interpolation is in $\mathcal{H}$ space for the principal curvatures at the critical points. Further details are described by Torrealba (2017).

We also consider limits for the tie lines at the critical point (i.e., critical tie lines),

$$\begin{aligned} \sigma_w^{cp} &= \begin{cases} \sigma_w^{III} & \mathcal{H} = \mathcal{H}_U \\ \sigma_{w,\infty}^{cp} & \mathcal{H} = -\infty \end{cases} \\ \sigma_o^{cp} &= \begin{cases} \sigma_o^{III} & \mathcal{H} = \mathcal{H}_L \\ \sigma_{o,\infty}^{cp} & \mathcal{H} = \infty. \end{cases} \end{aligned} \quad (18)$$

Using the same interpolation approach as in Eqns. 16-17, we obtain,

$$\begin{aligned} \sigma_w^{cp} &= \sigma_{w,\infty}^{cp} + A_{\sigma_w}^{cp} b_{H-} & -\infty < \mathcal{H} \leq \mathcal{H}_U \\ \sigma_o^{cp} &= \sigma_{o,\infty}^{cp} + A_{\sigma_o}^{cp} b_{H+} & \mathcal{H}_L \leq \mathcal{H} < \infty, \end{aligned} \quad (19)$$

where $A_{\sigma_w}^{cp}$ and $A_{\sigma_o}^{cp}$ are constants defined by evaluating Eqn. 19 at the corresponding $\mathcal{H}$ limits based on Eqn. 18.

For simplicity, we set $c_\infty^{cp-} \equiv c_{1,\infty}^{cp-} = c_{2,\infty}^{cp-}$ and $c_\infty^{cp+} \equiv c_{1,\infty}^{cp+} = c_{2,\infty}^{cp+}$. Then, the normalized tuning parameter for the principal curvatures can be defined as $\lambda_{cp-} = c_\infty^{cp-}/c_1^{III}(\mathcal{H}_U)$ and $\lambda_{cp+} = c_\infty^{cp+}/c_2^{III}(\mathcal{H}_L)$. Equivalently, the normalized tuning parameter for the critical tie lines can be defined as $\lambda_{cpw} = \sigma_{w,\infty}^{cp}/\sigma_w^{III}(\mathcal{H}_U)$ and $\lambda_{cpo} = \sigma_{o,\infty}^{cp}/\sigma_o^{III}(\mathcal{H}_L)$.

To summarize, in order to define the solubilization ratios we use Eqn. 3 in the type III region and Eqn. 8 in the type II- and type II+. The principal radii required to define Eqn. 8 (from Eqn. 6) are obtained by following the interpolation procedure shown in Appendix B. All model parameters (i.e., σ^* , $\mathcal{H}_U$, $\mathcal{H}_L$, λ_{cp-} , λ_{cp+} , λ_{cpw} , and λ_{cpo}) can be tuned to phase behavior data, as illustrated next. The resulting micellar geometries are illustrated in Fig. 2 for all microemulsion regions. Under the current interpolation procedure, the largest micellar radii ($r_{b,i}$) is calculated to be infinity in the two-phase lobes when the invariant point is in positive space (i.e., $\mathcal{H}_L \leq \mathcal{H} \leq \mathcal{H}_U$), which would be appropriate for systems with a small three-phase window ($\Delta\mathcal{H} = \mathcal{H}_U - \mathcal{H}_L$) such as those typically considered for EOR (optimum solubilization ratio is high).

The presented equation-of-state is consistent with the Gibbs phase rule: for a three-component, three-phase system, the microemulsion composition is determined by fixing two degrees of freedom (e.g., optimum solubilization and $\mathcal{H}$, or alternatively pressure and temperature) as shown in Eqn. 13. In the two-phase regions, an additional degree of freedom is gained, and here we must also specify a tie-line parameter. This is explained in detail in Appendix B.

3. Results

We now consider phase behavior estimates of the new curvature model and compare these against experimental data. The predictive capability of the model is shown by comparing its performance against phase behavior data for simultaneous changes in multiple formulation variables. Table 1 gives the model parameters for all cases considered.

3.1. Model properties

Case 1 is a hypothetical $\mathcal{H}$ -scan with an overall composition of $C_s = 0.02$ and a brine-oil-ratio of 1. Figure 3 (left) shows the principal curvatures, and Figure 3 (right) shows the corresponding spheroidal principal radii for the curvature model. When $c_1 > 0$ and $c_2 > 0$ both principal curvatures correspond to the oil micelles, and $r_{b,o} = 1/c_1$ and $r_{a,o} = 1/c_2$ (as used in the model in Eqns. 4-6). When $c_1 < 0$ and $c_2 < 0$ both principal curvatures correspond to the brine micelles, where $r_{a,w} = |1/c_1|$ and $r_{b,w} = |1/c_2|$. Finally, when $c_1 < 0$ and $c_2 > 0$, the positive principal curvature corresponds to the oil micelles and the negative principal curvature corresponds to the brine micelles, where $r_{a,w} = |1/c_1|$ and $r_{a,o} = 1/c_2$ (as used in Eqns. 9-10). For the radii to be representative, the value of c_c must be calibrated using scattering data for the system of interest. The behavior in Fig. 3 (right) is consistent with the observations of Kahlweit and Strey (1985) in the divergence of the correlation length determined by dynamic light scattering.

3.2. Model comparison for $\mathcal{H}$ -scan

Figure 4 shows phase behavior data for an oil—brine—sulfonate—tertiary amyl alcohol system as described by Salter (1977), and the corresponding curvatures from the model. Figure 4 (left) gives the solubilization ratios using Eqns. 4-8 and 13, while Fig. 4 (right) gives the corresponding phase volume fractions. The phase behavior data is accurately captured by the model, specifically the asymmetric phase transition boundaries and the three-phase data.

3.3. Model comparison for compositional data

Figure 5 shows compositional data for a decane—brine—AOT surfactant system as described by Lekkerkerker et al. (1996), and the corresponding curvature results. The model is able to capture accurately the location of the invariant point, as well as both two-phase lobes. For the type II+

lobe, the data is captured assuming the critical point is located in negative composition space, resulting in a non-vanishing tie-line length as the critical point is approached. This behavior is relevant for systems that exhibit phase separation between a micelle-rich and a micelle-poor phase as the critical point is approached (Kamei et al., 2002; Khorsandi and Johns, 2016).

3.4. Model predictability

Austad and Strand (1996) studied the three-phase oil and brine solubilization ratio as a function of both temperature and pressure for a variety of formulation scans for a sulfonate—dead oil—brine system. Let us define $G_o = \sigma_o^{III}(\mathcal{H}_U - \mathcal{H})/\mathcal{H}_U$ and $G_w = \sigma_w^{III}(\mathcal{H}_L - \mathcal{H})/\mathcal{H}_L$. If the model captures the data exactly, then $G_o = G_w = \sigma^*$ (under the assumption that optimum conditions is defined by $\sigma_o^{III} = \sigma_w^{III}$). This is a similar approach as described earlier by Torrealba and Johns (2017B) to test predictability. Figure 6 (left) shows σ^* versus G_o and G_w experimental results for six pressure scans at different optimum temperatures (ranging from 55 to 80°C) and six temperature scans at different optimum pressures (ranging from 50 to 300 bar). Figure 6 (right) shows the same data with the corresponding optimum pressure for temperature scans and optimum temperature for pressure scans, respectively. The data is consistent in that for similar optimum properties, the scans cluster around the same value. For example, the pressure scan data at optimum temperature of 80°C (with optimum pressure of 44.7 bar) clusters similarly compared to the temperature scan data at optimum pressure of 50 bar (with optimum temperature of 79.8°C).

Figure 7 (left) shows the relationship of pressure versus temperature at optimum condition. In order to predict phase behavior away from a single formulation variable scan, σ^* is correlated by the best fit plane to σ^* data in PT space as described previously (Torrealba and Johns, 2017B; Khorsandi and Johns, 2016). Relevant correlation parameters are shown in Table 2. Figure 7 (right) shows the predicted σ^* using the σ^* correlation, which yields accurate results. Combining the predicted values for optimum solubilization ratio, and using average H_U and H_L parameters (listed in Table 1), type III phase behavior is predicted for a number of temperature scans at different pressures (Figure 8, left) and pressure scans at different temperatures (Figure 8, right). The predictions agree well with experimental data.

3.5. Comparison with dynamic light scattering (DLS) data

Finally, we test the physical validity of our curvature-based model with dynamic light scattering (DLS) data. Figure 9 shows the correlation time data measured by DLS for a temperature scan of a $C_{4}E_2$ /cyclohexane/water system as described by Kahlweit and Strey (1985). Changes in temperature are plotted in terms of H . Following the simple scaling arguments from Appendix C, we are able to calculate the corresponding correlation time based on the curvature model from a definition of average micellar diameter (i.e., Eqn. C1). Then, under the assumption of constant average micellar velocity and appropriate integration, we derive two models: the ideal model that assumes the excess characteristic time (τ^E) is zero, and the non-ideal model that considers a non-zero τ^E to account for the deviation from constant average micellar velocity.

The results from both models in Fig. 9 show an accurate match to the data. Relevant parameters are listed in Table 3. In addition, we calculate the effective diameter corresponding to the correlation time data shown in Fig. 9 by using Eqn. C4 with the ideal and non-ideal parameters listed in Table 3. Figure 10 shows the inferred data and the corresponding average micellar diameter calculated from the curvature model, and the calculations again match the data well. This approach provides a simple method for estimating micellar sizes based on dynamic light scattering

data, and therefore it can help improve fluid characterization, which will impact phase behavior, interfacial tension, and viscosity (Torrealba and Johns, 2017).

4. Conclusions

We presented a curvature-based microemulsion phase behavior model based on spheroid micellar shapes that eliminates the use of NAC. This approach captures spherical, cylindrical and approximate bicontinuous micellar geometries using consistent equations to describe changes in curvatures across all Winsor regions. Some specific conclusions are:

- The model extends Torrealba and Johns (2017A) to define phase behavior directly using principal curvatures irrespective of interfacial tensions measurements availability.
- Micellar radii are estimated and can be calibrated using scattering data for a representative description of microstructural aspects of microemulsions.
- The model reproduces phase behavior from typical microemulsion experiments for scans in both $\mathcal{H}$ (at fixed overall composition) and composition (at fixed $\mathcal{H}$).
- Predictions from the new model are accurate when compared to an extensive data set of pressure and temperature scans.
- We validated the physical significance of our model by tying the correlation time obtained from dynamic light scattering to the mean micellar diameter. This result allows for an independent verification of the qualitative behavior of our curvature phase behavior model.

The model currently assumes monodispersity, and does not capture the periodicity of the micelles in the microemulsion (i.e., micelle-to-micelle distance). Extension of the model in these areas may be important if the model is to be coupled with processes where percolation around phase transitions are important, such as in microemulsion viscosity modeling.

Nomenclature

Roman

$A_{S,i}$	=	interfacial surface area for micelles of component i ($\text{\AA}^2$)
c	=	micellar curvature ($\text{\AA}^{-1}$)
c_c	=	constant related to the micellar curvatures ($\text{\AA}^{-1}$)
C_{ij}	=	volumetric concentration of component i in phase j (dimensionless)
C_m	=	mean curvature ($\text{\AA}^{-1}$)
d	=	Micellar diameter ($\text{\AA}$)
G	=	solubilization parameter for the curvature model (dimensionless)
$\mathcal{H}$	=	hydrophilic-lipophilic deviation (dimensionless)
HLB	=	hydrophilic-lipophilic balance (dimensionless)
HLD	=	hydrophilic-lipophilic deviation (dimensionless)
L	=	surfactant length ($\text{\AA}$)
PIT	=	phase inversion temperature ($^{\circ}\text{C}$)
r	=	micellar radii ($\text{\AA}$)
R	=	ratio of interactions (dimensionless)
S	=	micellar interface surface area ($\text{\AA}^2$)
V	=	volume (mL)

Greek

β_k	=	k-th constant in the correlation for predictions of σ^*
γ_{jk}	=	interfacial tension between phases j and k (mN/m)
λ_{cp-}	=	normalized tuning parameter for the principal curvatures in the type II- critical point (dimensionless)
λ_{cp+}	=	normalized tuning parameter for the principal curvatures in the type II+ critical point (dimensionless)
λ_{cpw}	=	normalized tuning parameter for the type II- critical tie line (dimensionless)
λ_{cpo}	=	normalized tuning parameter for the type II+ critical tie line (dimensionless)
v	=	Micellar speed ($\text{\AA}/\mu s$)
ξ	=	characteristic length scale ($\text{\AA}$)
σ_i	=	solubilization ratio of component i (dimensionless)
σ_i^o	=	ratio of total concentration of component i in the system to the total concentration of surfactant (dimensionless)
τ	=	characteristic time (μs)
Ω	=	scaling constant in Huh's equation (mN/m)

Subscripts

a	=	minor principal radii
b	=	major principal radii
D	=	Dimensionless
e	=	Effective
i	=	i th component
j	=	j th phase
k	=	k th phase
L	=	minimum lower limit
m	=	microemulsion phase
o	=	oil component or phase
s	=	surfactant component
U	=	maximum upper limit
w	=	brine component or phase
1	=	first principal curvature
2	=	second principal curvature
∞	=	limit as $ \mathcal{H} \rightarrow \infty$

Superscripts

E	=	excess property
i	=	i th component
i	=	curvature direction
*	=	optimum condition
III	=	three-phase
cp	=	critical point
–	=	type II- region
+	=	type II+ region

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Appendix A: Derivation of solubilization ratios in Winsor type III

In this Appendix we derive Eqns. 9 and 10. When $r_{b,i} \gg r_{a,i}$,

$$t^2 = 1 - r_{a,i}^2 / r_{b,i}^2 \rightarrow 1, \quad (A1)$$

so $t \rightarrow 1$ and $\sin^{-1} 1 \rightarrow \pi/2$. The area in Eqn. 5 then becomes,

$$A_{s,i} = 2\pi r_{a,i}^2 \left(1 + \frac{r_{b,i}}{2r_{a,i}} \pi \right). \quad (A2)$$

Further, within the parenthesis,

$$\frac{r_{b,i}}{2r_{a,i}} \pi \gg 1, \quad (A3)$$

such that,

$$A_{s,i} = 2\pi r_{a,i}^2 \left(\frac{r_{b,i}}{2r_{a,i}} \pi \right) = \pi^2 r_{a,i} r_{b,i} \quad (A4)$$

When Eqn. A4 is combined with Eqn. 4 and 7, we obtain the result for solubilization ratios in Winsor type III (Eqns. 9-10).

Appendix B: Interpolation of principal curvatures in two-phase regions

The interpolation procedure for type II- is illustrated in Figure 11 (top). The proposed interpolation procedure is based on the following transformation in Cartesian coordinates,

$$\begin{aligned} x &= C_o - C_w \\ y &= C_s, \end{aligned} \quad (B1)$$

but since $C_o = 1 - C_w - C_s$ for a ternary system, $x = 1 - 2C_w - C_s$. A tie line for a type II- region is given by $\sigma_w^\circ = C_w/C_s$. The equation for a tie line is given by,

$$x = 1 - y(2\sigma_w^\circ + 1). \quad (B2)$$

The reference critical point $v^{cp} = (x^{cp}, y^{cp})$ is obtained by finding the intersection of Eqn. A2 evaluated at $\sigma_w^\circ = \sigma_w^{cp}$ with $C_s = 1$ (i.e., $y = 1$). Therefore, the reference point is,

$$\begin{aligned} x^{cp} &= -2\sigma_w^{cp} \\ y^{cp} &= 1. \end{aligned} \quad (B3)$$

For $\mathcal{H}_L < \mathcal{H} < \mathcal{H}_U$, the reference point for the invariant point composition $v^{III} = (x^{III}, y^{III})$ is the intersection of Eqn. B2 evaluated at $\sigma_w^\circ = \sigma_w^{III}$ with $C_o = 0$ (i.e., $x = -1 + y$), and is given by,

$$\begin{aligned} x^{III} &= \frac{\sigma_w^{III}}{1 + \sigma_w^{III}} \\ y^{III} &= \frac{1}{1 + \sigma_w^{III}}. \end{aligned} \quad (B4)$$

For $\mathcal{H} \leq \mathcal{H}_L$ the invariant point is assumed to be at the pure brine apex (i.e., $v^{III} = (-1, 0)$), which is consistent with the interpolation procedure by Torrealba and Johns (2017A).

The straight-line through (x^{cp}, y^{cp}) and (x^{III}, y^{III}) is defined as,

$$x - x^{cp} = \theta_1 (y - y^{cp}), \quad (B5)$$

where $\theta_1 = (x^{III} - x^{cp})/(y^{III} - y^{cp})$. The reference point $v^\circ = (x^\circ, y^\circ)$ for an arbitrary tie line with σ_w° for which we want to estimate its principal curvatures is defined by the intersection of Eqns. B2 and B5,

$$\begin{aligned} x^\circ &= 1 - \theta_2(2\sigma_w^\circ + 1) \\ y^\circ &= \theta_2, \end{aligned} \quad (B6)$$

where $\theta_2 = (1 - x^{cp} + \theta_1 y^{cp})/(\theta_1 + 2\sigma_w^\circ + 1)$. The Euclidean distances d between v^{cp} and v^{III} , and d_1 between v^{cp} and v° are calculated by,

$$\begin{aligned} d &= \|v^{cp} - v^{III}\| \\ d_1 &= \|v^{cp} - v^\circ\|. \end{aligned} \quad (B7)$$

Finally, we define a weighting function $\lambda \equiv d_1/d$ so that the principal curvatures corresponding to a tie line with σ_w° is,

$$c_i^- = (1 - \lambda)c_i^{cp-} + \lambda c_i^{III} \quad i = 1, 2. \quad (B8)$$

The procedure for interpolating in a type III and type II+ system is analogous to the procedure described for a type II- system and is also illustrated in Figure 11.

Appendix C: Scaling between average micellar diameter to characteristic time from dynamic light scattering (DLS)

In this Appendix, we connect the time scale of intensity fluctuations (i.e., characteristic time) obtained from dynamic light scattering to the size of micellar aggregates. The effective diameter (d_e) of the prolate spheroid micelles in the microemulsion phase can be expressed by

$$d_e = \frac{2(r_a + r_b)}{2} = r_a + r_b. \quad (C1)$$

Assuming that the effective diameter (d_e) scales linearly with the correlation time constant (τ),

$$\frac{dd_e}{d\tau} = v, \quad (C2)$$

where v is the average micellar velocity or characteristic velocity. After appropriate integration, we obtain

$$d_e - d_{e,ref} = v(\tau - \tau_{ref}), \quad (C3)$$

which can be expressed by

$$\tau = \frac{d_e}{\nu} + \tau^E, \tag{C4}$$

with $\tau^E = \tau_{ref} - d_{e,ref}/\nu$ being the excess characteristic time for large-size micelles. Larger micelles would typically move slower; therefore, $\tau^E > 0$. For the ideal case, $\tau^E = 0$.

Figures and Tables

Figure 1. Behavior of the mean curvature of all micelles (C_m) with $\mathcal{H}$ for a fixed composition, as described by Strey (1994) for a temperature scan. The figure illustrates the locations of the type II-, type III, and type II+ regions.

Figure 2. Micellar geometry transitions using the prolate spheroid approximation model, with $\mathcal{H}$ increasing from left to right. From the left there are three oil internal micelles in the type II- region as the overall composition approaches the type III region. Next, three bicontinuous micelles are illustrated in the type III region, with $\mathcal{H} = 0$ for the center case. Finally, we show three water internal micelles in the type II+ region as the overall composition recedes from the type III region.

Figure 3. Principal curvatures using the interpolation procedure (left) and corresponding principal spheroid radii (right) versus $\mathcal{H}$ in the curvature model at fixed composition. The figures illustrate the location of the different Winsor phase behavior regions. As the overall composition enters the type III region, one of the principal curvatures vanishes, making the corresponding principal radius diverge, which demarks the onset of bicontinuity.

Figure 4. Experimental data of phase behavior and curvature model results for an $\mathcal{H}$ -scan: Oil and water solubilization ratios modeled using Eqns. 4-8 and 13 (left), and corresponding phase volume fractions (right). Data is for fixed overall composition from Salter (1977).

Figure 5. Ternary diagram showing comparison of experimental data and the tuned curvature model for a composition scan using decane at 40°C for a fixed $\mathcal{H}$. Experimental data from Lekkerkerker et al. (1996).

Figure 6. Experimental σ^* versus G (as defined in section 3.4) for different temperature and pressure scans (left) and accompanying optimum data for reference (triangles). The same data is shown (right) with their corresponding optimum pressure (for temperature scans) and optimum temperature (for pressure scans). Data from Austad and Strand (1996).

Figure 7. Pressure versus temperature at optimum condition (left) and corresponding experimental σ^* versus predictions for the same temperature and pressure scans (right). Data from Austad and Strand (1996).

Figure 8. Type III phase behavior predictions for different temperature scans at varying pressures (left) and different pressure scans at varying temperatures (right). Data from Austad and Strand (1996).

Figure 9. Correlation time determined by dynamic light scattering data, and results obtained by the curvature model combined with the development shown in the Appendix C using Eq. C4 for the ideal and the non-ideal cases. Data from Kahlweit and Strey (1985).

Figure 10. Effective diameter data inferred from the correlation time data for ideal and non-ideal cases, and results obtained by the curvature model. Data from Kahlweit and Strey (1985).

Figure 11. Illustration of key elements in the interpolation procedure for determining principal curvatures for type II- (a), type II- lobe in type III (b), type II+ lobe in type III (c) and type II+ (d) environments.

Table 1. Curvature model parameters for all cases considered.

Data set	σ^*	$\mathcal{H}_U$	$\mathcal{H}_L$	λ_{cp-}	λ_{cp+}	λ_{cpw}	λ_{cpo}
Case 1	10.0	0.5	-0.5	0	0	-1	-1
Salter (1977)	11.4	0.90	-0.35	1	1	-15	-1
Lekkerkerker et al. (1996)	8.2	0.08	-1.03	0	0	-6.5	-2
Austad and Strand (1996)	-	0.43	-0.23	-	-	-	-
Kahlweit and Strey (1985)	3	0.08	-0.075	0	1	-10	-10

Table 2. Tuned correlation parameters for σ^* predictions.

Data set	$\beta_1, ^\circ C^{-1}$	β_2, bar^{-1}	β_3
σ^* , Austad and Strand (1996)	-0.667	-0.042	64.83

Table 3. Correlation time parameters.

Case	$\nu, \text{\AA}/\mu s$	$\tau^E, \mu s$
Kahlweit and Strey (1985): ideal case	15	0
Kahlweit and Strey (1985): non-ideal case	45	45