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Ternary Phase Diagrams for Surfactant/Oil/Brine Mixtures

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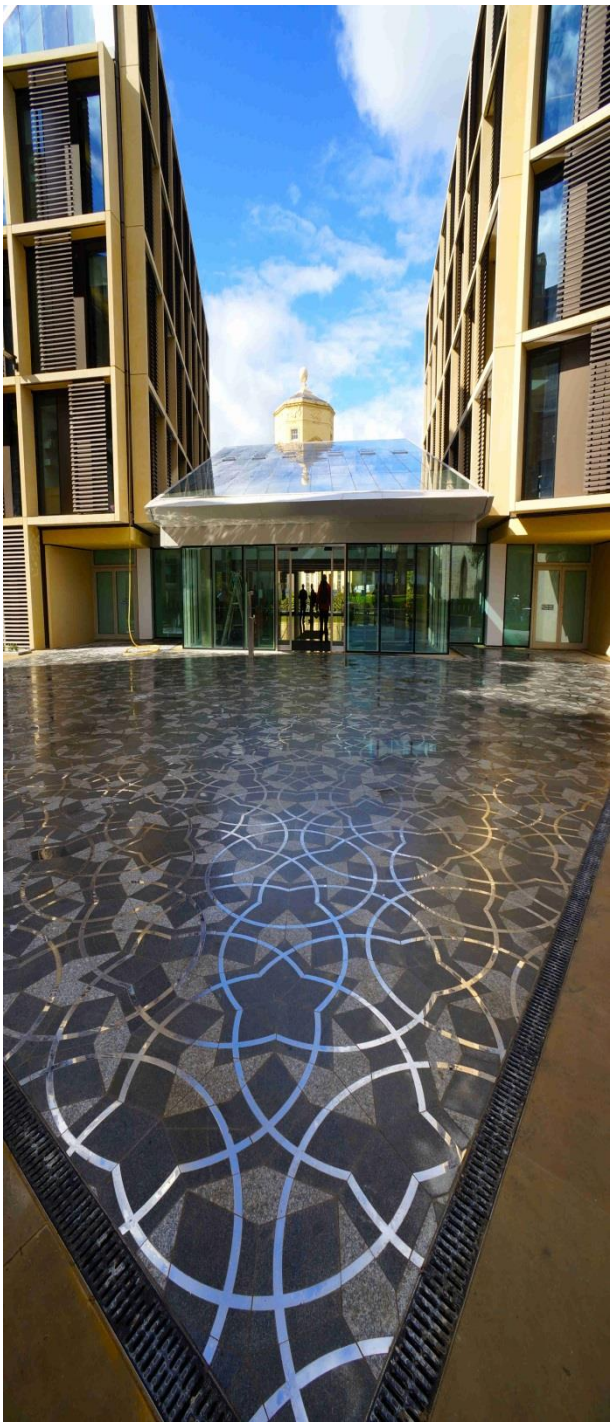
Schlumberger



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1. Introduction

The production of hydrocarbons (oil and gas) from underground reservoirs is typically achieved by injecting water (typically brine) at a distance from the production well in order to force the hydrocarbons through the formation to the surface. This process becomes inefficient as water injection progresses, and can result in substantial amounts of the oil being left behind in the porous rock formations of the reservoir. This is because oil and water are immiscible, and so the water flow can bypass the liquid oil in the rock formation, leaving it trapped in the rock.

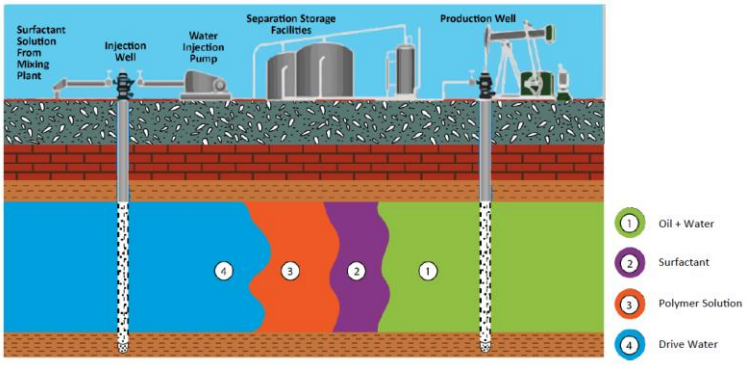


Figure 1: Schematic diagram of an oil reservoir. An oil recovery mixture is injected underground to mobilize the oil that is trapped. Source: Primera Reservoir

Surfactants are detergent-like chemicals that facilitate the fine mixing of oil and water (emulsion).

Among the enhanced oil recovery techniques employed to improve this performance is the use of surfactant, a detergent-like chemical, in the injected brine (see figure 1). Surfactant makes oil and water much more miscible, therefore improving the amount of oil recovered.

Due to the costs involved in drilling wells, and the possibility of leaving the oil in a state that is more difficult to remove after initial attempts of extraction, oil companies normally use reservoir simulators to calculate the expected performance of different scenarios of well placement and scheduling of fluid injection. These simulators must, among other things, include the tendency of the fluids to form different phases. Without the presence of surfactant, these phases are simply oil and water (we neglect the presence of gas). With surfactant present, the fluids do not simply mix into one phase but can form multiple phases with different structures, which affect the efficiency of production. This is represented in a simulator through a phase transition model.

Schlumberger have built commercial reservoir simulators which use a phase transition model called the *Hand's Rule* [1]. They are interested in comparing this model to a new model called HLD-NAC [2] (we will describe these two models on page 4). The HLD-NAC model has a much greater emphasis on the physical modelling of how the phases are formed than Hand's Rule. However, earlier investigations by Schlumberger suggest that this model predicts very different phase behaviours from those observed experimentally. Our aim is to give a critical assessment of, and comparison between these two models. In particular, we will focus on understanding how the HLD-NAC model behaves under different assumptions about the input parameters and how these are related to its predictions of phase behaviour.

2. Predicting Phase Behaviours

Surfactant molecules have a head that prefers to reside in the water phase and a tail that prefers to reside in the oil phase. Thus, surfactant molecules adsorb at oil-water interfaces.

It is possible to characterise surfactant-oil-brine (SOB) systems using three primary *schemes*, as described and labelled by Winsor [3]. In the Winsor I scheme, the oil is suspended as droplets in the water. The oil is stabilised against reforming as a single phase by the surfactant molecules. The resulting suspension of small oil droplets in a water phase is known as an oil-in-water micro-emulsion: it is stable and does not tend to unmix. Winsor I also includes the presence of an excess oil-only phase. The corresponding Winsor II scheme has a water-in-oil micro-emulsion (water droplets suspended in oil), with an excess water-only phase.

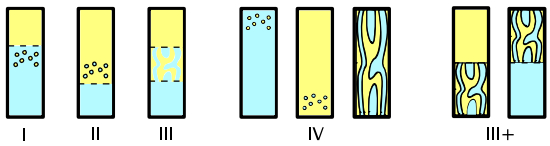


Figure 2: Schematic representation for surfactant-oil-brine (SOB) systems that are in equilibrium in different Winsor schemes. Oil (yellow) resides above brine (blue).

Mixing different amount of surfactant, oil, and brine together can generate different types of emulsion

For the Winsor III scheme, water and oil exist in extended laminae in the micro-emulsion phase. In this region, water and oil are separated by a single-molecule layer of surfactant, oriented between the phases in the same way as in the other Winsor schemes. In addition to this region, there is an excess oil-only phase and a water-only phase present. There are two further schemes: Winsor IV corresponds to any of the previous schemes with only the micro-emulsion phase present, and Winsor III+ corresponds to Winsor III with only a single excess phase. The Winsor schemes are illustrated in figure 2.

Ternary phase diagram

We can describe an SOB mixture using the volume fractions of its three components: oil, brine, and surfactant. In some studies, the 'surfactant' is made up from a combination of surfactant molecules and alcohol, with a fixed volume ratio between the two; in others, the alcohol content of the overall mixture is a fixed value, while the surfactant is allowed to vary. The alcohol, an optional component, acts as a co-surfactant. Its purpose is to boost the surfactant performance by helping to remove oil and debris from the rock surface. Ternary diagrams are used to describe how the mixture behaviour varies as the component fractions change. We assign the volume fraction of a component of the system to each axis of the ternary diagram and mark each mixture as a point on the diagram. The coordinates of each point sum to unity. The information each point displays is colour-labelled, as illustrated in figure 3, and shows the phase state of the overall mixture.

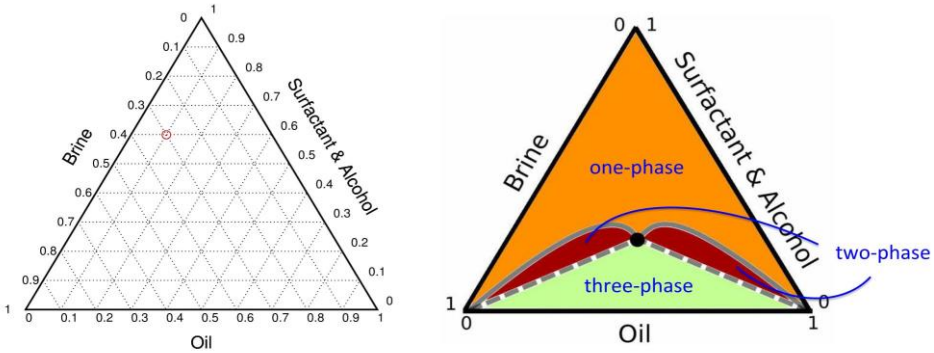


Figure 3: Ternary diagrams for a surfactant-oil-brine (SOB) system. (left) The coordinate system. The point that is marked in red has volume fractions (Surfactant & Alcohol, Oil, Brine) = (0.6, 0.1, 0.3). (right) The standard empirical understanding of a typical output for a ternary phase diagram. Colours are used to indicate systems with different number of phases.

A natural choice of labelling these points is by their Winsor schemes. The phase diagram exhibits a rich topology, with the diagram being partitioned into regions, for example as in figure 3. With this diagram, we are able to identify phase transitions as the mixture changes

its composition at different parts of a reservoir.

However, generating a phase diagram by experimental measurement can be impractical due to the number of mixtures that have to be sampled. Furthermore, the plot's topology is unique to the properties of each component and can change substantially with the external environment, such as temperature, and other mixture properties, such as the brine salinity. Therefore, it is desirable to construct a mathematical model which can physically predict the Winsor scheme and what each region contains, for any given mixture.

Mathematical models

Hand's Rule model. In the absence of alcohol, experimental observations suggest that the phase behaviour follows that shown in figure 3. The two-phase regions, shown in red in figure 3, start at the all-brine and all-oil corners of the diagram, and terminate at a common 'central' point. Above these regions is a single-phase SOB mixture and below them is a triangular Winsor III three-phase region. The position of the common central point varies with the salinity of the system. By assuming that the diagram has such a topology, Hand's Rule [1], which is an experimentally based rule, predicts phase composition by imposing the observation that certain ratios between relative volume fractions of components in the same phase satisfy a power law relationship. However, this model requires some experimental information (on volume fractions and the position of the central point) as inputs, and the equations are computationally demanding to solve, due to their iterative nature.

HLD-NAC model. The Hydrophilic-Lipophilic Difference (HLD) is a dimensionless quantity which measures whether a surfactant prefers to be in brine or oil: it is calculated by an explicit semi-empirical formula [2]. HLD is a function of salinity, temperature, molecular structure of the oil, surfactant, and also the alcohol concentration. The Net-Average Curvature (NAC) model describes the curvature of the interface of the surfactant-filled phase, where we assume the hypothetical coexistence of uniform, spherical droplets of oil and brine in the micro-emulsion phase [3]. The model further assumes that there is a critical length scale for this curvature beyond which Winsor III type micro-emulsion will occur. We use these equations to predict how much oil or brine has been emulsified, and hence whether excess phases will form. In this case, there is no prescribed topology of the ternary phase diagram – each point's phase properties are calculated separately from a deterministic physical model.

3. Predictions from the HLD-NAC Model

In order to analyse the ternary phase diagram outputs from the HLD-NAC model, we first qualitatively compare these outputs with the known ternary diagram topologies, for the special case where alcohol is absent. This is because there is no universal convention on how the surfactant component is defined on a ternary diagram for systems that contain alcohol, as mentioned in Section 2. Furthermore, ternary diagrams that are currently used for implementing the Hand's Rule model in the reservoir simulators are plotted with alcohol being absent or at a fixed concentration.

When alcohol is absent, the HLD-NAC model generates phase diagrams that agree with experimental observations

In the absence of alcohol, the HLD does not vary with composition. In Figure 4, we present the ternary diagrams that have been generated by the model at different salinities. This is in good agreement with the expected behaviour, in terms of having a triangular region for Winsor III and two two-phase lobes on each side of the triangle. Furthermore, as salinity increases, the central point exhibits the same behaviour of moving across the diagram, from left to right. The central point moves from the full-brine apex to the full-oil apex of the diagram; at these salinity extremes, the three-phase region is absent.

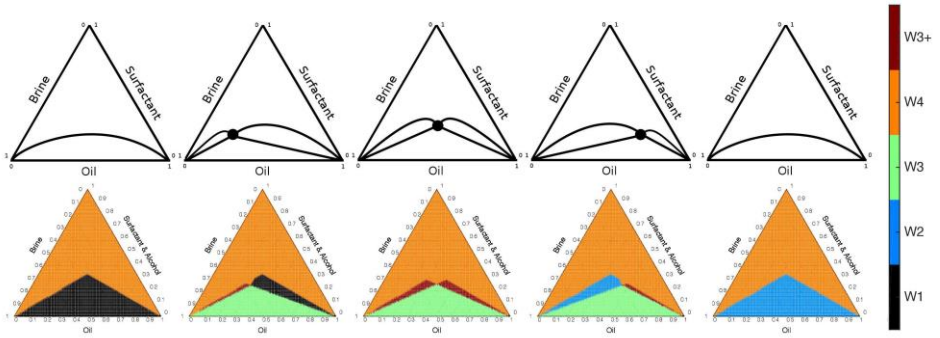
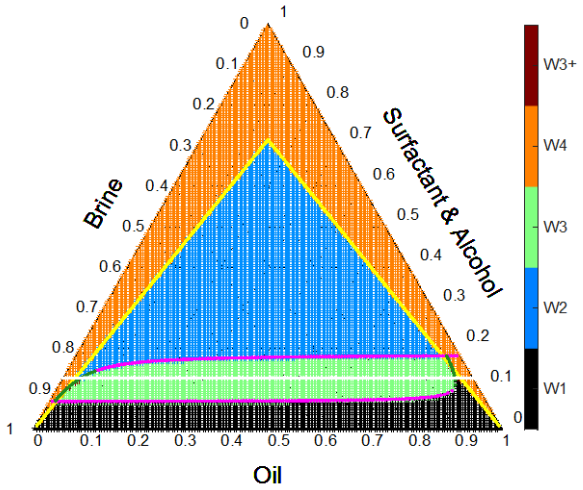


Figure 4: Typical ternary phase diagrams with salinity increasing from left to right, when alcohol is absent. Schematic diagrams along the top row indicate the expected behaviour [2], with solid lines indicating that adjacent regions differ in the number of phases and black circles indicating the central point of each diagram. The bottom row displays predictions with the HLD-NAC model. Colours indicate different Winsor schemes, as shown in the colour bar.

Influence of alcohol

When generating the diagrams in figure 4, we assumed that the alcohol is absent at all points, but alternative topologies are possible when alcohol is present. In the case where there is a constant amount of alcohol as the surfactant fraction varies, the resulting diagrams are similar to those obtained with zero alcohol as shown in figure 4. We focus our attention on the behaviour when the surfactant and alcohol are mixed at constant ratio. The resulting diagram is shown in figure 5. In this case, as the amount of surfactant is



varied, the alcohol concentration also changes.

Figure 5: Typical output of a ternary diagram with a surfactant-alcohol ratio of 1:4. The white line indicates the compositions where HLD = 0 and other solid lines indicate mathematical bounds between regions with different Winsor schemes.

As noted in Section 2, given constant oil and surfactant properties and constant salinity, HLD only varies with the alcohol concentration according to a semi-empirical formula. As a result, constant horizontal lines (constant surfactant-plus-alcohol concentration) in the ternary diagram are now contours of constant HLD. In particular, the HLD = 0 line (shown in white in figure 5) horizontally bisects the Winsor III region in the centre of the diagram. We have developed a detailed mathematical examination of the HLD-NAC model, which provides an analytical form for the phase boundary lines in figure 5, which separate the Winsor III region from the Winsor I and II regions (shown in pink in figure 5) and from the Winsor III+ regions (shown in dark green). Finally, the single-phase boundary is shown in yellow.

We can predict the feasibility of Winsor III by determining four dimensionless parameters (A, r, β, and λ)

Our examination of the model has predicted that there are upper and lower bounds on the salinity of the brine beyond which Winsor III is infeasible. The bounds are determined by four key dimensionless parameters: A, a mass ratio between the molecular weight of the surfactant and the total mass of the surfactant molecules that occupy a unit area of the oil-water interface; r, the proportion of surfactant in the surfactant-alcohol mixture; β, the ratio between the tail-length of the surfactant molecule and the critical length scale for Winsor III, and λ, a characteristic parameter for alcohol, which must be obtained experimentally. This knowledge will be particularly useful in selecting mixture compositions for enhanced oil recovery.

When HLD is constant, corresponding to the case when the alcohol content is independent of the amount of surfactant, or is absent, our analysis simplifies and we find that the phase boundary lines are reduced to straight lines, as seen in Figure 4.

Effect of solubility of alcohol

Experimental results indicate that the distribution of alcohol should take into account of its solubility

The amount of alcohol solubilised in each phase is an important determinant of phase composition. Initial estimates of the HLD-NAC phase behaviour assumed equipartitioning of the alcohol between oil and brine. However, alcohol can partition non-equally, depending on its solubility in each phase. We use a partition coefficient to describe the ratio between the amount of alcohol in the oil and in the brine. Experimental evidence suggests that, at low salinity and alcohol concetration, the partition coefficient will be much smaller than unity, implying that most of the alcohol will be solubilised in water. However, for sufficiently high salinity and/or concentration of alcohol, the brine becomes saturated with alcohol and most of the alcohol will be solubilised in oil. This is shown in figure 6 (left), where we plot the partition coefficient using the data from [4]. We incorporate partitioning into the HLD-NAC model, and then use this improved model to predict the position of the phase interfaces in a test tube model, for which Schlumberger has experiemental data. We show the results in figure 6 (right), where we see that the incorporation of partitioning improves the prediction of the phase interfaces.

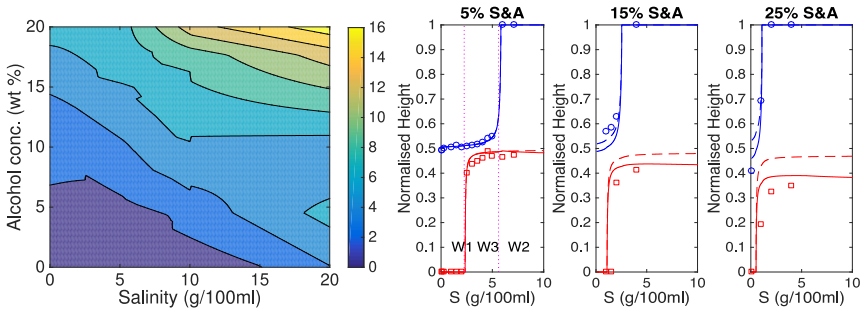


Figure 6: Alcohol partitioning between oil and brine. (left) Partition coefficient as a function of alcohol concentration and salinity of the brine. Data is taken from [4]. (right) The location of the top (blue) and bottom (red) interface between different phases (in a test tube), at different concentrations of the surfactant-alcohol component. Predictions of the HLD-NAC model are shown as dashed lines (equipartition) and solid lines (partition coefficient). The experimental data is shown as circles or squares.

4. Discussion, Conclusions & Recommendations

We have analysed the predictions of phase behaviours for SOB systems made using the HLD-NAC model, and shown how to represent such results via Winsor schemes and ternary phase diagrams. We have demonstrated that there are qualitative similarities between the outputs of this model and experimental observations in the absence of alcohol. The roles of alcohol and surfactant-alcohol ratio have also been proven to be crucial in interpreting alternative ternary diagram results where the surfactant-alcohol ratio is varied.

We also investigated the effect of incorporating alcohol partitioning between the brine and oil phases; the modified model has better agreement with experimental data. This provides improved understanding of how the role of alcohol should best incorporated into the model, when it is implemented in reservoir simulators. By providing mathematical expressions for outlining the phase boundaries, we have enabled easier phase boundary detection when using the HLD-NAC model (since this model does not prescribe the ternary diagram topology). In summary, we have provided an increased insight into how the diagrams should be used and interpreted for applications in enhanced oil recovery.

Extending the model

The HLD-NAC model was originally developed for mixtures with low surfactant concentrations. In order to capture the physics at high surfactant concentrations, we have made the simple assumption that single-phase micro-emulsion (Winsor IV) occurs when there is more surfactant present than either oil or brine. This condition should be refined to give more accurate phase boundaries, but its presence is important in providing the boundaries between the single-phase (Winsor IV) and two-phase regions (Winsor I, II, or III+) seen in figure 4 and 5. Without this, the two-phase regions extend much further up the diagram, which is unphysical. Although a high surfactant concentration is impractical for applications in enhanced oil recovery, due to the associated cost, this condition should be refined in the future for the completeness of ternary diagram outputs.

5. Potential Impact

The physically motivated HLD-NAC model provides a simple method for predicting phase behaviours and compositions for surfactant-oil-brine mixtures. Its robustness, which we have verified, is useful in accelerating or improving the resolution of current reservoir simulations where phase compositions have to be calculated at every time step in multiple locations.

Chris Marooney, Senior Software Engineer at Schlumberger, commented

"*Modelling the role of surfactant in simulations of enhanced oil recovery is an important part of our contribution to oilfield operations. The HLD-NAC model is a newer tool which requires understanding of how it relates to existing modelling, in order to deploy it correctly and advise customers on its application. Clint has provided a very thorough analysis of how the model behaves and what are the critical behaviours which should be considered in order to use it correctly so that it agrees with our empirical understanding of the surfactant-oil-brine system. This enlightening investigation into the properties of the HLD-NAC model will significantly enhance the way we use and develop it. Schlumberger are considering implementing the HLD-NAC model in a commercial simulator in a medium-long time scale.*"

References

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