The Utility of HLD/NAC to Guide Surfactant Selection and Design

Introduction

A surfactant/oil/water microemulsion is a complex system. The phase behavior of such systems (including transitions, solubilizations, and their dependencies on various factors, such as salinity, fluid properties, temperature, and surfactant characteristics) is extremely complex to accurately capture and properly describe. Different models have been proposed in attempts to describe and predict microemulsions phase-behavior (Robertson, 1988). Winsor provided the most significant contribution. His classification of microemulsions phase-behavior into 4-types has been widely adopted in many fields or applications. For instance, in surfactant enhanced oil recovery (EOR), the highest IFT reduction is achieved in the Winsor Type-III region (Lake, 1988). Achieving this minimum IFT requires thorough studies to design ideal surfactant formulations. Such ideal – but not necessarily optimal or practical – formulations would yield the highest capillary number and hence the biggest residual oil mobilization due to capillary desaturation. With a clear understanding of a given surfactant phase-behavior, we can design and optimize injection slugs for EOR applications to assure the realization and maximum maintenance of a Winsor Type-III system across the displacing fronts. Such understanding is traditionally achieved through salinity-scanning phase-behavior experiments. The results are often unique to a given reservoir. Hence, such efforts are revisited for every new case.

The Hydrophilic-Lipophilic Difference and Net-Average Curvature (HLD/NAC) model was suggested to offer the necessary understanding for the design of surfactant formulations and injection slugs. In other words, HLD/NAC could offer an alternate approach. At the least, HLD/NAC could optimize the screening process (Torrealba et al. 2018). HLD/NAC is basically an equation of state (EOS) for microemulsions. In theory at least, it provides significant improvement over earlier surfactant phase-behavior modeling attempts and at last offers a reliable EOS in terms of phase-behavior predictions that matches actual experimental observations. The model has different assumptions that were introduced to enhance its prediction power (Torrealba et al. 2018). The model origin stems from the Hydrophilic-Lipophilic difference (HLD) equation which was derived by Salager et al. (1979). They derived and demonstrated HLD utility for prediction of surfactant systems optimal conditions. In 2003, Acosta et al. introduced the NAC component which allows the reproduction of key information such as solubilization, phase transitions, and interfacial tension. Ghosh and Johns (2016) extended the HLD/NAC model to account for pressure effects. According to them, their new extended HLD/NAC model can help design chemical EOR. In Ghosh and Johns (2018), this potential utility was better framed to the modeling of phase behavior for more robust reservoir simulation. In reservoir simulation, current surfactant models are practically (AlSofi et al., 2013) and unnecessarily (AlSofi and AIKhatib, 2014) complex, and yet of little predictive power (Ghosh and Johns, 2016).

However, in addition to use in reservoir simulation, recent studies suggest HLD/NAC potential utility for the design of surfactant formulations (Jin et al., 2017; Wang et al., 2019). In general, for any model to be of value in design and optimization, it needs to offer a reasonable degree of uniqueness. Therefore, in this work, we investigate this aspect—i.e. we focus on the uniqueness of HLD/NAC parameters with respect to their predictions. For that purpose, we use an in-house Matlab-based HLD/NAC simulator. We firstly use the simulator to generate the HLD/NAC base parameters. Those are generated by fitting experimental solubilization-data. We then perform single- and multivariate sensitivity analyses to investigate the uniqueness of the HLD/NAC parameters. In this process, we study the ranges of different-parameters that would offer acceptable prediction of the experimental results.

Methodology

In layman terms, HLD/NAC consider the key parameters to capture solubilization in terms of ratios, volumes and transitions. An in-house Matlab-based HLD/NAC simulator was used. In this simulator (Figure 1), three surfactant parameters (surfactant head-area, length and molecular weight) are used to model the phase behavior as a function of brine salinity. Those parameters are generated by fitting the HLD/NAC solubilization predictions to inputted observations. The main inputs in terms of observations...
are the solubilization ratios as a function of salinity. Additional inputs characterizing the oil/brine/surfactant system are necessary and include: the oil equivalent alkaline carbon number (EACN), water-oil ratio, total volume, and surfactant concentration.

**Base Model Prediction.** We use solubilization ratios published in the literature as base observations. Ranges for each of the three surfactant parameters is assumed. With that, the software estimates the three surfactant parameters by minimizing the error in solubilization ratios (i.e. between HLD/NAC predictions and inputted laboratory observations).

**Univariate Sensitivity.** The in-house Matlab HLD/NAC simulator has a built-in univariate sensitivity module. The module allows comparison of the base solubilization curves against those that would be obtained by a different value of any of the three surfactant parameters. We use this module to investigate the sensitivity of the phase-behavior predictions with respect to the three surfactant parameters. For each parameter, we obtain the range that would maintain reasonable predictions of solubilization-curves with respect to the inputted laboratory data. Such range or window would then reflect the uniqueness of the model in terms of the three surfactant parameters; and hence, the HLD/NAC model utility with respect to guiding surfactant design.

**Multivariate Sensitivity.** To conduct a multivariate sensitivity, we again – for each parameter – obtain the range that would maintain reasonable predictions of solubilization-curves with respect to the inputted laboratory data. However, we do this, by fixing one of the three surfactant parameters at the minimum and maximum bounds obtained in the univariate sensitivity. Prior to sensitivity analyses on the other two parameters, a modified set of optimal values for them are obtained. Such results would further reflect the overall degree of uniqueness of the HLD/NAC model.

**Figure 1**—User interface of the Matlab-based HLD/NAC simulator illustrating some of the key inputs.

**Results and Discussion**

**Base Model Prediction.** The base surfactant model was obtained based on fitting solubilization data. The predicted solubilization curves against inputted laboratory observations are plotted in **Figure 2a**. The based model surfactant parameters are listed in **Table 1**.

**Univariate Sensitivity.** The results of the univariate sensitivity are also summarized in Table 1. Clearly, relatively wide ranges of all three surfactant parameters can be afforded. Within each parameter window, the HLD/NAC predictions deviate slightly and hence still provide a reasonable fit (**Figure 2a**). Outside the window, the fit quality deteriorates (**Figure 2b**).
**Multivariate Sensitivity.** The changes in optimal surfactant parameters as one of the three parameters is fixed at the minimum or maximum bounds are also listed in Table 1. With such optimization, the remaining surfactant parameters vary moderately but more importantly, the quality of the obtained solubilization fits are improved. The results of the additional sensitivities performed at those bounds are summarized in Table 1, too. As expected, the acceptable window for each parameters increases slightly compared to those observed in the univariate sensitivity.

These results support the non-uniqueness of the three surfactant characteristics. Accordingly, and at least in its current form of implementation, the HLD/NAC model doesn’t seem capable of guiding the selection, design and/or optimization of surfactant formulations for EOR applications.

![Figure 2](image)

**Figure 2**—HLD/NAC example results: inputted laboratory data (○), base predictions (–), and sensitivity results (···): (a) at a parameter maximum bound, and (b) outside a parameter maximum bound.

<table>
<thead>
<tr>
<th>Case</th>
<th>Molecular Weight (g/mol)</th>
<th>Surface Area (Å)</th>
<th>Surfactant Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Model</strong></td>
<td>604</td>
<td>62.8</td>
<td>90</td>
</tr>
<tr>
<td><strong>Single Variable Sensitivity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at Lowest Molecular Weight</td>
<td>294, 872</td>
<td>40, 130</td>
<td>25, 105</td>
</tr>
<tr>
<td>at Highest Molecular Weight</td>
<td>400, 1100</td>
<td>45, 120</td>
<td>45, 120</td>
</tr>
<tr>
<td>at Lowest Surface Area</td>
<td>250, 700</td>
<td>50, 145</td>
<td>25, 90</td>
</tr>
<tr>
<td>at Highest Surface Area</td>
<td>400, 1100</td>
<td>45, 125</td>
<td>60</td>
</tr>
<tr>
<td>at Lowest Surface Length</td>
<td>200, 550</td>
<td>45, 120</td>
<td>40</td>
</tr>
<tr>
<td>at Highest Surface length</td>
<td>350, 1100</td>
<td>45, 125</td>
<td>60</td>
</tr>
<tr>
<td><strong>Multivariate Sensitivity - Overall</strong></td>
<td>200, 1100</td>
<td>30, 145</td>
<td>25, 120</td>
</tr>
</tbody>
</table>

**Table 1**—Multivariate sensitivity: Changes in parameters optimal value and their reasonable for a given shift in one parameter within single-sensitivity bounds.
Conclusion

In this work, we use an in-house HLD/NAC model coded in Matlab to investigate the utility and power of HLD/NAC EOS to guide the screening and design of surfactants for EOR applications. We focus on the predictions of solubilization ratios since they reflect the system key characteristics. We investigate the utility of the model from a uniqueness standpoint. Basically, the HLD/NAC model requires different input parameters, such as the surfactant concentration, surface area, length and molecular weight, to predict the system phase behavior.

We use laboratory based phase behavior data to study the bounds and uniqueness of surfactant surface area, length, and molecular weight (surfactant 3-characteristics). The laboratory-based solubilization curves are firstly fitted by the software; a step that provides the optimal values of the surfactant 3-characteristics. Later, we perform univariate and multivariate sensitivity studies. The results demonstrate the uniqueness attached to each of the surfactant 3-characteristics. Large bounds were observed in the univariate and multivariate sensitivity. For example, while an optimal fit is obtained with a surfactant length of 63 A, lengths between 30 and 145 A still yield solubilization predictions that reasonably match laboratory-based data. This range is within the likely variations of surfactants. Similar findings were observed for the other characteristics: molecular weight and surface area.

Thus, the results of this work demonstrate the need to carefully constrain the HLD/NAC model to attain uniqueness and hence generate a model that is suitable to guide the selection and design of surfactants.

References


