

Automating Surfactant Design for Enhanced Oil Recovery: Accelerating Innovation in Oil and Gas Industry

Vai Yee Hon¹, Ivy Chai Ching Hsia¹, Noor 'Aliaa Amira M Fauzi¹, Estelle Deguillard², Jan van Male²,
Jan-Willem Handgraaf²

¹PETRONAS

Kajang, Selangor, Malaysia

honvaiyee@petronas.com.my; ivy_chai@petronas.com.my

²SIEMENS Culgi

Leiden, Netherlands

estelle.deguillard@siemens.com

Abstract - Designing a robust surfactant formulation for chemical enhanced oil recovery (EOR) application in oil and gas industry is challenging and robust. Speed and accuracy at design stage are critical. This work presents a novel methodology distinguished by its highly automated workflow, which combines patent search, analysis, structure generation, simulation and analysis to revolutionize surfactant design for enhanced oil recovery. At its core, this work utilizes computational chemistry simulations as the primary tool for surfactant development, eliminating the need for resource-intensive experimental testing. The main goal is to measure interfacial properties and uncover insights into the intricate relationship between molecule composition, structural modifications, and oil recovery potential. This dramatic paradigm shift holds the promise of accelerating chemical development by an astounding 90%. This study is a good illustration of the difficulty behind designing a surfactant from patent information. It revolves around the automated creation and optimization of surfactant structures gathered from relevant patents. The automated pipeline generates multiple structure candidates from each patent, then systematically investigating the influence of different factors on surfactant efficacy. Together with the automated molecule parameterization, new molecules are quickly created within an hour, while simulations can be halted based on early data assessment. The structure can then be directly redesigned using the learnt information from the computation. Therefore, this iterative approach enables rapid refinements on several molecules based on computational insights in a single day. The study's remarkable outcomes are rooted in its automated design prowess. Automation remains at the forefront even when dealing with complex patent information. By harnessing the power of automation, researchers can expedite the design and testing of novel chemicals for diverse applications, spanning from oil production to demulsification.

Keywords: surfactant, enhanced oil recovery, emulsion, computational chemistry

1. Introduction

Traditionally, the development of chemical EOR formulations has relied heavily on empirical experimentation, which is both time-consuming and resource intensive. The formulation of effective surfactant generating Type III phase behavior microemulsion for a specific crude composition remains a challenge. However, recent advancements in computational chemistry enables researchers to gain insights into molecular interactions between surfactant and crude oil components for design and optimization of CEOR surfactant formulations. From molecular dynamics simulations to Dissipative Particle Dynamics (DPD) and beyond, computational tools provide a virtual laboratory for studying the complex physicochemical interactions between surfactants, brine and crude oil at atomistic level. Furthermore, the scalability and versatility of these computational methods allow for rapid screening of a vast chemical space, accelerating the discovery of novel surfactant formulations.

In this context, this paper first introduces the methodology to assess microemulsion behavior and implement in Dissipative Particle Dynamics (DPD) simulation. Then it examines the surfactant structures selected from patents, providing insights into the chemical compositions and structural characteristics of these surfactant with the associated microemulsion phase behavior. It demonstrates that by systematically exploring variations in chemical fragments and tail compositions of

surfactants, researchers can identify structure-property relationships and design promising surfactant structures for further investigation.

2. Methodology

At first, a physics-based model to assess the formation of microemulsion at optimum condition at molecular level was established. The model is developed based on a comprehensive understanding of the physical chemistry of microemulsion interfacial tension and torque concepts [1]. Winsor [2] described that an optimal microemulsion (Type III phase behavior) is formed when the microstructure surface is flat, i.e. $R = 1$. When $R < 1$, there is a tendency to form oil-in-water emulsion (Type II- phase behavior), whereas when $R > 1$, the tendency is to form water-in-oil emulsion (Type II+ phase behavior).

Secondly, microemulsion structure is governed by the elastic constants, the bending rigidity, k and the saddle splay modulus, k_s [3]. Bending rigidity characterizes the resistance of the interface towards bending. Bending rigidity was obtained by analyzing the undulation spectrum of the microemulsion interface. The approach is based on hypotheses from Rekvig et al. [4] using equipartition principal and fast fourier transform (FFT) application to decomposes the undulation signal into different wave lengths. It was used to estimate the microemulsion interface bending rigidity to deduce interface stability and surfactant solubility.

Next, both models for assessment of microemulsion phase behavior and bending rigidity were implemented using DPD simulation method. DPD is a coarse-grained molecular dynamics technique that simplifies molecular representations by modeling them as beads. It simulates molecular interactions governed by Newton's equations, incorporating conservative, dissipative, and random forces. It can automate molecule generation, parameterization, and conduct coarse-grained molecular dynamics simulations. Additionally, it facilitates thermodynamic computations essential for understanding the complex microemulsion systems.

Lastly, by leveraging on Derwent World Patents Index and PatBase global patent database, patents with distinct surfactant structures are shortlisted according to the relevant patent classification (Table 1) to analyze their composition and molecular characteristics as potentially effective chemical EOR surfactants.

Table 1: Relevant classification for patent refinement.

| No | Classification | | Details |
|----|--|-----------|--|
| 1 | International Patent Classification (IPC) | C09K8/584 | Compositions for Enhanced Oil Recovery characterized by the use of surfactants |
| 2 | | E21B43 | Methods or apparatus for obtaining oil |
| 3 | Cooperation Patent Classification (CPC) | C09K8/284 | Compositions for Enhanced Oil Recovery characterized by the use of surfactants |
| 4 | | E21B43 | Methods or apparatus for obtaining oil |
| 5 | United States Patent Classification (USPC) | 507/938 | Enhanced oil recovery with microemulsion |

3. Results and Discussion

For this study, we conducted a patent search on the technology of “surfactants for enhanced oil recovery.” A total of 282 base set of patents emerged from the initial search. We then refine the base patent set to 28 patents by applying the relevant classification. Eventually, we manually selected 3 patents featuring surfactant structures deemed promising for EOR. Note that the patent status was not taken into account in this study. These 3 patents covering various surfactant types, spanning amphoteric, multicarboxylate, and Gemini variants.

3.1. Amphoteric Surfactant

The first patent [6] claims the following structure (Fig. 1):

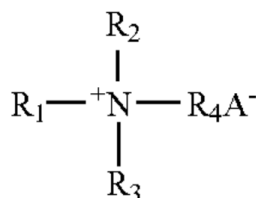


Fig. 1: Amphoteric surfactant chemical structure claimed in patent US7556098B2

where R_1 is hydrocarbyl group or alkyl amido group, R_2 and R_3 are hydrocarbyl or alkoxy group, R_4 is aliphatic group and A is carboxylate or sulfonate group.

That patent claims that the carboxylate group can also be a sulfonate group. We then investigate the impact of sulfonate group on the overall behaviour of the surfactant at the interface. However, simulations revealed instability at the interface for the sulfonate-headed surfactant. Due to the interface instability, it was unable to obtain the microemulsion phase behavior and the associated bending rigidity. In short, although the sulfonate head group notably enhanced oil solubility, it failed to confer interface stability, highlighting the delicate balance required in surfactant design.

3.2. Multicarboxylate Surfactant

The second patent [7] claims the structure of a multicarboxylate surfactant (Fig. 2):



Fig. 2: Multicarboxylate surfactant chemical structure claimed in patent EP 2924092A1

where R_1 is branched or unbranched, saturated, or unsaturated, cyclic, or non-cyclic, 7 to 150 carbon atoms, R_2 is at least one ethylene oxide (EO), propylene oxide (PO), butylene oxide (BO), or a combination, and R_3 is branched or unbranched carbon chain, 2 to 12 carbon atoms, 2 to 5 COOH groups. A systematic analysis of various multicarboxylate surfactant structures, categorized into EO, PO, and EO-PO types were conducted to discern tail elongation's impact on water solubility counterbalance. It was observed that adding of PO groups has negative impact on the phase behavior but increases the bending rigidity. The structures with 2 PO groups tends to form micelles in water, indicating that these surfactants are too water soluble. Meanwhile, by increasing the number of EO groups shows better phase behavior and increases the bending rigidity. This indicates potential good surfactants that can generate Type III stable optimal microemulsion at low concentration.

3.3. Gemini Surfactant

The third selected patent [8] claims the following (Fig. 3) Gemini surfactant structure:

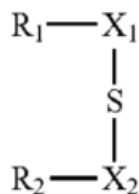


Fig. 3: Gemini type surfactant chemical structure claimed in patent WO2011106287A1

where R_1 and R_2 can be CC, -CC=CC-, C#C, -COC-, -CCO-, with at least 16 carbon atoms, both R_1 and R_2 can be identical or not, X_1 and X_2 can be P, S, SO₃, -C(=O)O, both X_1 and X_2 can be identical or not, and S is a spacer in between X_1 and X_2 with CC, -CC=CC-, C#C, or aromatic consisting 2 to 12 carbon atoms, note that # is a triple bond.

The investigation into Gemini surfactants focused on tail composition's influence. Simulations show that they formed stable structure at interface with very high bending rigidity. This indicates that they could have low solubility although these surfactant structures are relatively easy synthesis. Meanwhile, surfactants with tails comprising solely carbon atoms exhibited increased in oil solubility, while those incorporating EO groups favoured water solubility. A structure with a balanced alkane chain and EO groups could be a promising candidate for further exploration.

Overall, a total of 25 structures were evaluated in this study. Among these 25 structures, 12 were shortlisted for further investigation. Eventually, only 1 structure manifested both desirable phase behavior and bending rigidity values, warranting synthesis and experimental validation. The total simulation time for this study is approximately 1 month. In comparison with laboratory synthesis work, it would require about 25 months to complete.

4. Conclusion

This study emphasizes the role of computational chemistry in surfactant design for chemical EOR applications. Utilizing physics-based models to assess microemulsion phase behavior and stability, novel surfactant structures were systematically screened and evaluated. This study demonstrated the complexity of designing a surfactant that can sustain a stable and optimum interface. A subtle structural modification can have significant effects on the final properties of a surfactant. This validated computational chemistry approach offers a rapid screening and design platform for novel surfactant structures. The streamlined process, from molecule design to properties assessment results in over 90%-time reduction in new molecule design, demonstrating the efficiency gains made possible by computational chemistry.

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