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## Design and Evaluation of Efficient Microemulsion System for Chemical EOR

Shehzad-Ahmed, K. A. Elraies and Shuaib Ahmed Khalwar  
Petroleum Engineering Programme, Faculty of Geoscience and Petroleum Engineering,  
Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak, Malaysia

**Abstract:** Microemulsion behavior is an important aspect in chemical EOR because these can be used as an indicator for ultra low interfacial tension. At optimal salinity, type III microemulsion begins to form by solubilizing equal volume of aqueous phase and oil phase in the middle phase. However, salinity lower or higher than optimal causes significant increase in the interfacial tension, resulting in insufficient displacement efficiency. In this study, the behavior of microemulsion is investigated experimentally. Type III microemulsion were generated at different salinities using surfactant, co-surfactant, alcohol and crude oil to form gel and liquid crystal free clear microemulsion. As a result, alcohol alkoxy sulfates has shown good performance in term of solubilization for light oil and low temperature conditions. Effect of varying surfactant, co-surfactant and co-solvent concentration on microemulsion parameter has been presented. This systematic approach helps in efficient formulation screening and optimization of chemical EOR formulation in order to achieve ultra low interfacial tension between the residual oil and injection water.

**Key words:** EOR, microemulsion, solubilization, oil recovery

### INTRODUCTION

Enhance oil recovery is used after secondary recovery to target the remaining immobile oil in water swept zones. This remained upswept oil is due to capillary pressure and IFT between brine and crude oil. Surfactant flooding has been found the best technique to achieve ultra low IFT.

In surfactant flooding, surfactant interacts with crude oil and brine to form microemulsion (Lake, 1989; Green and Willhite 1998). Understanding of this interaction of surfactant with crude oil and brine is very important in order to move towards better recovery efficiency. In 1954, Winsor classified microemulsion into three types i.e., type I (oil in water), type III (bicontinuous) and type II (water in oil) (Zhao *et al.*, 2008; Flaaten *et al.*, 2009; Puerto *et al.*, 2010; Sheng, 2010). At intermediate salinity type III microemulsion begin to form and this special type of microemulsion has been found most suitable for achieving ultra low IFT (Healy *et al.*, 1976; Pope *et al.*, 1982; Aoudia *et al.*, 1995; Flaaten *et al.*, 2008; Hirasaki *et al.*, 2011). Therefore, phase behavior tests are performed to quickly evaluate the favorable formulation for surfactant flooding (Nelson and Pope, 1978; Flaaten *et al.*, 2008). Phase behavior experiments tell about microemulsion parameter i.e., optimal solubilization and optimal salinity and according to Huh equation optimal solubilization is

inversely related to IFT (Flaaten *et al.*, 2008; Zhao *et al.*, 2008; Hirasaki *et al.*, 2011).

In this study, an experimental methodology is adapted to test and screen the selected chemicals in phase behavior experiments. On the basis of microemulsion parameter, commercial surfactants i.e. Alcohol Alkoxy Sulfate (AAS) and Internal Olefin Sulfonate (IOS) were screened with lighter crude. Effect of chemical types and concentration on microemulsion parameter such as optimal solubilization ratio, optimal salinity and equilibrium time is investigated.

### MATERIALS AND METHODS

A strategic methodology was used to examine the phase behavior of microemulsion. Various concentrations of surfactant, co-surfactant and co-solvent were used in order to achieve type III microemulsion and to study their effect on microemulsion phase behavior. This strategic methodology has efficiently evaluated the chemicals interaction with crude oil and with each other in obtaining the desired type III microemulsion. The performance of formulation was monitored by comparing microemulsion parameters i.e., optimal solubilization ratio, optimal salinity and equilibrium time. Formulation showing good optimal solubilization ratio, less equilibrium time and less viscous microemulsion was selected as the best formulation.

**Corresponding Author:** Shehzad-Ahmed, Petroleum Engineering Programme, Faculty of Geoscience and Petroleum Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak, Malaysia  
Tel: +601116660832

**Material description:** Apparatus used in this study includes borosilicate pipettes, pipettes stand, flame torch, weighing balance and convection oven. All the phase behavior experiments were conducted with lighter crude at 60°C. Chemicals used in this study are discussed below:

Two Alcohol Alkoxy Sulfates (AAS) i.e., A771 and J771 provided by Shell were used in this study. A771 and J771 have two different carbon chains (i.e., C12-13 and C16-17, respectively) 7 Propylene Oxide (PO) and a sulfate group. Shell also provided their Enordet 0332, a commercial Internal Olefin Sulfonate (IOS) surfactant having twin tailed hydrophobe with 14 to 16 carbon atoms and a sulfonate group attached to its head. Alpha Olefin Sulfonate (AOS) used in this study was supplied by Stepan and another surfactant i.e. sodium dodecyl sulfate (SDS) was supplied by Sigma Aldrich. Co-solvent used is Secondary Butyl Alcohol (SBA) and an electrolyte i.e., NaCl was also used in all phase behavior experiments.

**Phase behavior experiments:** In phase behavior experiments, different surfactants, co-surfactants and a co-solvent were screened to design an optimized formulation. Array of pipettes were prepared using different combination of surfactant, co-surfactant, co-solvent and different incremental electrolyte (i.e., NaCl) concentration to monitor the change in the microemulsion data (such as oil and water volume solubilized) at various salinity increments. Equal volume of crude oil was then added in the pipettes. Pipettes were sealed by heating using flame torch, slowly tilted several time to mix aqueous and oil phase properly and then allowed to place pipettes in vertical position in oven at 60°C for the settlement of phases. Volume of phases were observed and recorded over time by inspecting visually and salinity was also recorded where cloudiness or separation of phases take place.

Prior to the addition of crude oil, aqueous phases were inspected visually in order to check the homogeneity and clarity of added chemicals with brine. It has indicated the compatibility of surfactants and co-surfactant with brine.

Phase behavior experiments were performed at various salinity increments to obtain clear picture of microemulsion types. Firstly coarse salinity increment was used to find optimal salinity region and then finer increments was used to focus in on middle phase region for more accurate measurement. Oil and water solubilization ratios (i.e.,  $V_o/V_s$  and  $V_w/V_s$ ) were calculated by measuring the volume of oil and water in microemulsion. Plot of oil and water solubilization ratio verses salinity has given two curves and intersection of these two curves gives optimal salinity and optimal solubilization ratio.

## RESULTS AND DISCUSSION

**Phase behavior results:** Number of Phase behavior experiments was performed by changing surfactant, co-surfactant and co-solvent concentration in order to design an optimum formulation. After accessing aqueous stability tests, surfactant/co-surfactant/co-solvent formulations were checked by criteria which include low viscosity microemulsion, less equilibrium time and high oil and water solubilization ratio.

Commercial surfactants and co-surfactants with concentration ranging from 1 to 4 wt% and 0 to 1 wt%, respectively were used with light Malaysian crude. Alcohol alkoxy sulfate with two different carbon chains (i.e., C12-13 AAS and C16-17 AAS) have shown good solubilization ratio and hence indicating ultra low IFT.

Initially phase behavior experiments performed with C12-13 AAS at low co-solvent concentration has given some cloudiness or milky phases and macroemulsion was observed in the pipettes. With the increase of co-solvent concentration these cloudy and milky phases disappeared. At 6 wt% SBA clear microemulsion was obtained as shown in Fig. 1.

Phase behavior pipettes prepared at two different C12-13AAS concentrations and 6 wt% SBA are shown in Fig. 1. It can be seen by comparing Fig. 1a, b, that with the reduction of surfactant concentration, volume of type III microemulsion is decreased. C12-13 AAS surfactant has shown good solubilization due to presence of PO groups and matching of surfactant chain length with light crude oil. While comparing the solubilization plot in Fig. 2a, b, it is clear that solubilization ratio is increasing with the increase of surfactant concentration. Effect of co-solvent concentration can also be seen by comparing solubilization plot of same surfactant but different co-solvent concentration as shown in Fig. 2b, c. From the comparison it is clear that optimal solubilization ratio is high for low co-solvent concentration and vice versa (Sheng, 2010).

Co-surfactants tested is IOS which has shown very good performance by giving clear less viscous microemulsion with reduced equilibrium time i.e., 1 day (Flaaten *et al.*, 2008; Puerto *et al.*, 2010). Co-surfactant has increased optimal salinity value to 4.75 wt%, whereas it has reduced optimal solubilization ratio.

Another surfactant i.e., C16-17 AAS has also given good performance. This is due to its chain length compatibility with crude oil and presence of 7 PO groups in its structure (Leung and Shah, 1987; Flaaten *et al.*, 2008). From the solubilization plot of 2 wt% C16-17 AAS and 6 wt% SBA shown in Fig. 2d, it can be seen that solubilization ratio is 12 which is quite favorable for achieving ultra low IFT. At low co-solvent concentration C16-17 AAS has given cloudy and milky

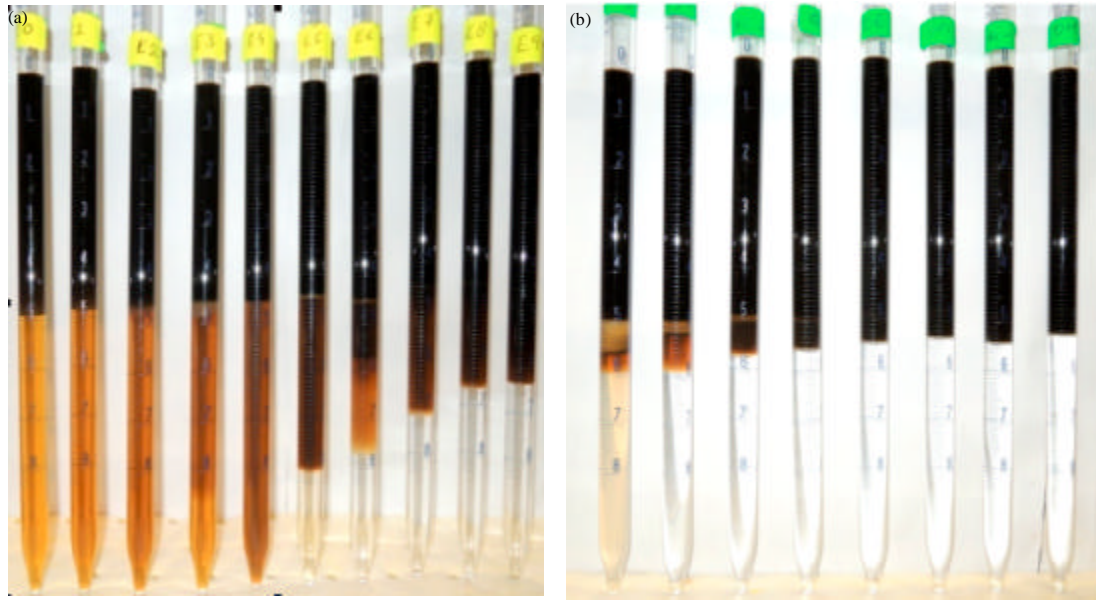


Fig. 1(a-b): Phase behavior pipettes with increasing NaCl concentration from left to right, (a) 4 wt% C12-13 AAS and 6 wt% SBA, (b) 1 wt% C12-13 AAS and 6 wt% SBA

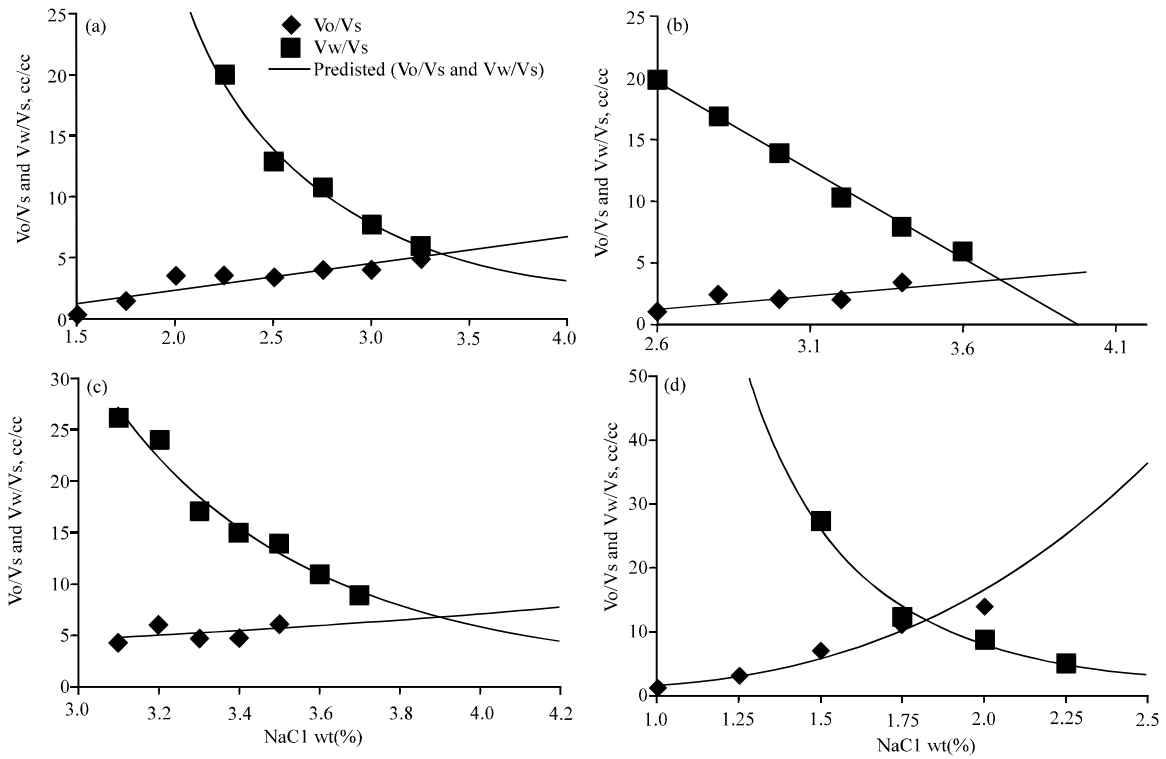


Fig. 2(a-d): Oil and water solubilization curves for (a) 4 wt% C12-13 AAS and 6 wt% SBA, (b) 1 wt% C12-13 AAS and 6 wt% SBA, (c) 1 wt% C12-13 AAS and 4 wt% SBA and (d) 2 wt% C16-17 AAS and 6 wt% SBA

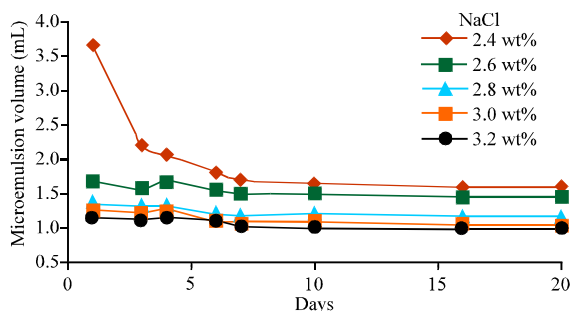


Fig. 3: Type III Microemulsion volume verses time of 2 wt % C12-13 AAS and 6 wt% SBA

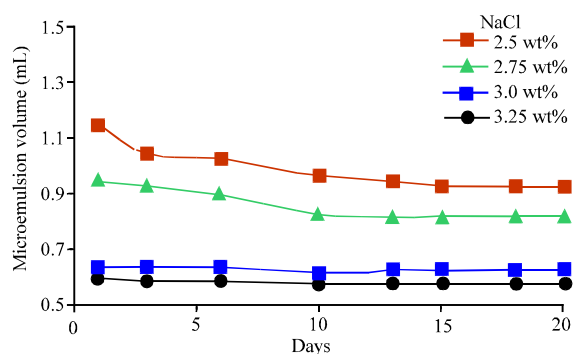


Fig. 4: Microemulsion volume verses time of Type III microemulsion of 3 wt% C12-13 AAS and 6 wt% SBA

aqueous phases showing little solubilization of oil in aqueous phase but no microemulsion was observed. However, as co-solvent concentration was increased, cloudy and milky phases started disappearing mean while at 6 wt% SBA clear microemulsion was obtained.

**Type III microemulsion volume and equilibrium time:**

Type III microemulsion volume in all phase behavior pipettes at various salinities were observed and recorded over time. Plots of type III microemulsion volume verses time of phase behavior experiment performed at two different surfactant concentration (i.e., 2 and 3 wt% C12-13 AAS) and 6 wt% SBA for different type III salinities are shown in Fig. 3 and 4, respectively. Volume of microemulsion was found decreasing with time which becomes constant after several days. The time after which microemulsion volume remains constant is the equilibrium time. It is observed that type III microemulsions prepared with 2 wt% surfactant at all the salinities stabilize after 10 days which is the equilibrium time for this particular formulation as shown in Fig. 3. When the surfactant concentration was increased to 3 wt%, equilibrium time was found to be 15 days. However for 1 wt% surfactant,

equilibrium time observed was reduced to 5 days. Hence it is clear that equilibrium time increases with the increase of surfactant concentration.

Observation from Fig. 3 and 4 indicates that for a particular surfactant concentration, type III microemulsion at high salinity stabilize faster as compared to type III microemulsion at low salinity and vice versa. Rate of change of microemulsion volume for low salinity type III microemulsion is high as compared to high salinity type III microemulsion. It can also be seen from Fig. 3 and 4 that microemulsion volume reduces with the increase of salinity. This reduction of microemulsion volume is due to decrease of repulsive forces between micelles of surfactant, which causes them to come close to each other rapidly as vander wall forces become predominant (Kumar and Mittal, 1999).

**CONCLUSION**

Phase behavior experiments provide rapid inexpensive laboratory approach for optimizing large number of chemical formulation prior to core flooding. Number of phase behavior experiments performed has efficiently evaluated chemicals and their interaction with each other and with crude oil. General screening of various high performance surfactants are made with light crude. Increase of surfactant concentration has increased the optimal solubilization ratio, whereas increase of co-solvent concentration has given less viscous clear microemulsion. Equilibrium time increases with increase of surfactant concentration and decreases with the increase of co-solvent concentration. Microemulsion volume reduces with time till equilibrium time and remains constant after equilibrium. For a particular formulation, type III microemulsion at high salinity stabilize faster as compared to type III microemulsion at low salinity.

Alpha olefin sulfonate and internal olefin sulfonate have shown good salinity tolerance but low oil solubilization. IOS has increased optimal salinity and reduced the viscosity of microemulsion and hence proved itself as good co-surfactant. Phase behavior experiments performed has shown that alcohol alkoxy sulfate gives good performance with light Malaysian crude oil by giving high oil solubilization ratio, less equilibrium time and less viscous microemulsion.

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