Prediction of optimum salinity and solubilization ratio for microemulsion phase behavior with live crude at reservoir pressure

M. Roshanfekr [a], R.T. Johns [b],*

[a] The University of Texas at Austin, Petroleum and Geosystems Engineering, 1 University Station C0300, Austin, TX 78712-0228, USA
[b] The Pennsylvania State University, Energy and Mining Engineering, 119 Hosler Building, University Park, PA 16802, USA

ARTICLE INFO

ABSTRACT

Reservoir pressure and solution gas can significantly alter the microemulsion phase behavior and the design of a surfactant-polymer flood. This paper shows how to predict changes in optimum salinity and solubilization ratio from dead oil at atmospheric pressure to live crude at reservoir pressure. Our method requires obtaining only a few glass pipette measurements of microemulsion phase behavior at atmospheric pressure and reservoir temperature. The key finding is that at reservoir pressure the optimum solubilization ratio and the logarithm of optimal salinity behave linearly with equivalent alkane carbon number (EACN). These trends are predicted from the experimental data at atmospheric pressure based on density calculations of pure components using the Peng–Robinson equation-of-state (PREOS). We show that predictions of the optimum conditions for live oils are in good agreement with the few experimental measurements that are available in the literature. We also present new measurements at atmospheric pressure to verify the established trends.

1. Introduction

A successful surfactant-polymer (SP) flood relies on achieving ultra-low interfacial tension (IFT) to increase the capillary number and mobilize the residual oil saturation trapped by capillary forces. The IFT between the microemulsion and brine phases must also be low to avoid trapping the microemulsion phase during the subsequent polymer drive. The salinity plays an important role in achieving low IFT between both the microemulsion and oil, and the microemulsion and brine. The optimum salinity is defined as the salinity where the IFTs are equal (Healy et al. [1]). Huh [2] derived a theoretical, but very practical equation showing that the interfacial tension varies inversely as the square of the solubilization ratio at atmospheric pressure. Thus, the optimal salinity is alternatively defined as the salinity where the solubilization ratios for brine and oil are equal. The optimum condition depends on the oil composition, salinity, pressure, temperature, and properties of surfactant/co-surfactant/co-solvent. Selection of appropriate surfactant and polymer for EOR purposes has been addressed by Levitt et al. [3] and Levitt and Pope [4].

Very few experiments of microemulsion phase behavior with live oils at pressure have been done. A live oil contains dissolved gas at reservoir pressure, while a dead oil at atmospheric pressure has lost its lighter oil fractions. Nelson [5] was one of the first who examined the effect of pressure on the microemulsion phase behavior using an anionic surfactant. He did one experiment at constant salinity and observed that diluting stock tank oil with methane at higher pressure increased the oil solubilization ratio. He did not, however, examine the effect of methane content and pressure on the optimal salinity.

Puerto and Reed [6] did the first systematic study of the effect of pressure and methane on microemulsion phase behavior using salinity scans. They observed that when oil is pressurized with methane, the optimum salinity decreases, while the optimum solubilization ratio is increased. They proposed that a surfactant/oil/brine system can be modeled by three parameters: optimum salinity, optimum solubilization ratio and oil molar volume. However, they concluded that their approach could not predict the optimum conditions for oils containing light hydrocarbons.

There have been several microemulsion phase behavior measurements for dead oil at elevated pressure. Kahlweit et al. [7] and Sassen et al. [8] showed that the type III invariant point (microemulsion composition in the three-phase region) on a ternary diagram for dead oil shifted towards type II- as pressure increased. Skauge and Fotland [9] also studied the effect of pressure on microemulsion phase behavior with heptane. They showed that pressure increases

the optimum salinity with heptane, but decreases its optimum solubilization ratio. More importantly, they showed that the optimum salinity with heptane at high pressure is correlated to density instead of molar volume.

Austad and Strand [10] and Austad et al. [11] added a constant mole fraction of methane to synthetic oil and measured the water and oil solubilization ratio changes with pressure at constant salinity. They showed that the optimum pressure (pressure at which the solubilization ratios are equal at constant salinity) increased as methane was added to the oil.

Roshanfekr et al. [12] recently examined separately the effect of pressure and methane on the microemulsion phase behavior. They demonstrated that the optimum salinity for a fixed oil composition increases with increasing pressure, while the optimum solubilization ratio decreases with pressure. The addition of methane at constant pressure decreases the optimum salinity, while increasing the optimum solubilization ratio. They also developed a thermodynamic proof that at constant salinity, temperature, and oil composition, the logarithm of oil and water solublities are linear functions of pressure. They further showed using UTCHEM (Delshad et al. [13] and Delshad et al. [14]), a chemical flooding simulator, that the shift in the optimum salinity can be very important to the proper design of a surfactant-polymer flood.

Shouthwick et al. [15] carried out microemulsion phase behavior experiments on live crude and observed that the live oil optimum salinity is decreased and the optimum solubilization ratio increased compared to dead crude oil at atmospheric pressure. Using regular solution theory, they predicted that optimum solubilization ratio will not always increase upon addition of methane to dead oil. However they did not provide any experimental evidence for their prediction.

Knudsen et al. [16] attempted to model the effect of pressure on Winsor type II and III microemulsion phase behavior using a cubic EOS with modified mixing rules. Their EOS model, however, was not successful in predicting the three-phase region as pressure changed.

A more successful approach in predicting optimum salinities is based on the equivalent alkane carbon number (EACN) concept initially proposed by Cayias et al. [17] and Cash et al. [18]. Salager et al. [19] demonstrated a linear relationship between the logarithm of optimum salinity and EACN at atmospheric pressure. Graciaa et al. [20] further showed that the trend of optimum solubilization ratio versus EACN is also nearly linear. Many authors, however, stated that the EACN concept does not apply for EACN oils below about five (Cayias et al. [17], Nelson [5]).

In this paper we show how to correct the EACN concept to higher pressures to predict the optimum conditions for EACN oils that contain methane. We first start by giving new experimental results for pure alkanes at atmospheric pressure to identify trends in the optimum parameters as a function of the EACN for the surfactants selected. The Peng–Robinson equation-of-state is used to calculate the densities to convert the EACN trend to higher pressures. Last, we demonstrate that the EACN concept for live oils can correctly predict the optimum conditions (salinity and solubilization ratio) when applied at the reservoir pressure of interest. We use three live oil experiments reported in the literature to validate the EACN approach.

2. Experimental material

Experiments were performed at atmospheric pressure (and at expected reservoir temperature) to identify the optimal salinity and solubilization ratio as a function of the EACN for a dead crude labeled here as oil A. The optimum conditions for this crude with methane are given by Roshanfekr et al. [12].

Table 1
Synthetic oil brine (SOB) composition.

Salt	Concentration (g/L)
NaCl	114.46
CaCl$_2$	15.54

Table 2
Synthetic hard brine A (SHB A) composition.

Salt	Concentration (g/L)
NaCl	0.035
KCl	0.099
MgCl$_2$·6H$_2$O	0.160
CaCl$_2$	0.099

Table 3
Synthetic hard brine B (SHB B) composition.

Salt	Concentration (g/L)
NaCl	0.122
CaCl$_2$·2H$_2$O	0.150
MgCl$_2$·6H$_2$O	0.203
CaSO$_4$	0.106

The phase behavior experiments used surfactants and brine being considered for a surfactant-polymer flood. The surfactant stock consisted of iso-tridecyl propoxylated sulfate (TDA-13PO-SO$_4$) with 83 wt.% active matter. The co-surfactant used was an internal olefin sulfonate (C$_{15-18}$IOS) with 23 wt.% active matter; the co-solvent was research grade isobutyl alcohol (IBA) in that its purity is greater than 99.5%. We used three different pure alkanes; octane, decane and dodecane, which were also research grade. Three brines were prepared with deionized water, one of which was prepared from research grade NaCl, and CaCl$_2$ (labeled SOB for synthetic oil brine), and the second brine from NaCl, CaCl$_2$, MgCl$_2$·6H$_2$O and KCl (labeled SHB A for synthetic hard brine A). The third brine consisted of NaCl, CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O and CaSO$_4$KCl (labeled SHB B for synthetic hard brine B). Tables 1–3 give the compositions of these brines. The SHB A brine contains only 0.03 wt.% total dissolved solids, the SHB B brine is 0.06 wt.% dissolved solids and the SOB brine is 13 wt.% total dissolved solids.

3. Experimental method

We started the experiments by sealing and labeling the 5 ml borosilicate pipettes. The narrow ends of the pipettes were sealed with a flame torch. Each pipette was labeled with the desired surfactant/co-surfactant/co-solvent concentration, SOB concentration, water–oil ratio, and the type of oil.

A stock solution of surfactant, co-surfactant and co-solvent was then prepared in the correct proportions to achieve the wt.% that is twice what is desired for the final wt.%. 1.0 ml of stock solution was placed into the pipette and diluted with a total volume of 1.0 ml of the relatively fresh SHB A solution and the SOB brine. The proportion of the SHB A and SOB volumes used depends on the desired salinity. At the end of this step the pipette contained 2 ml of surfactant, co-surfactant, co-solvent, and brine in the desired proportions. The aqueous solution level was recorded on the pipette and then 2 ml of a dyed alkane was added to the solution to give a water–oil ratio of 1.0. The oil is dyed red so that we can differentiate between the aqueous and oil phases.

Once the fluids were placed in the pipette we used Argon gas to displace air out from the top of the pipettes. The use of Argon minimizes the amount of air dissolved in the liquids. The pipettes were then sealed with a flame torch.