ABSTRACT

Chung, Jaeyub. Ph.D., Purdue University, December 2020. Interfacial Tension and Phase Behavior of Oil/Aqueous Systems with Applications to Enhanced Oil Recovery. Major Professor: Bryan W. Boudouris and Elias I. Franses

Chemical enhanced oil recovery (cEOR) aims to increase the oil recovery of mature oil fields, using aqueous solutions of surfactants and polymers, to mobilize trapped oil and maintain production. The interfacial tensions (IFTs) between the injected aqueous solution, the oil droplets in reservoirs, and other possible phases formed (e.g., a "middle phase" microemulsion) are important for designing and assessing a chemical formulation. Ultralow IFTs, less than 10^{-2} mN·m^{-1}, are needed to increase the capillary number and help mobilize trapped oil droplets. Despite this fact, phase behavior tests have received more attention than IFTs for designing and evaluating surfactant formulations that result in high oil recovery efficiencies, because incorporating reliable IFTs into such evaluation process is avoided due to difficulties in obtaining reliable values. Hence, the main thrusts of this dissertation are to: (a) develop robust IFT measurement protocols for obtaining reliable IFTs regardless of the complexity of water and oil phase constituents and (b) improve the existing surfactant polymer formulation evaluation and screening processes by successfully incorporating the IFT as one of the critical parameters.

First, two robust tensiometry protocols using the known emerging bubble method (EBM) and the spinning bubble method (SBM) were demonstrated, for determining accurately equilibrium surface tensions (ESTs) and equilibrium IFTs (EIFTs). The protocols are used for measuring the dynamic surface tensions (DSTs), determining the steady state values, and establishing the stability of the steady state values by applying small surface area perturbations by monitoring the ST or IFT relaxation behavior. The perturbations were applied by abruptly expanding or compressing surface areas by changing the bubble sizes with an automated dispenser for the EBM, and by altering the rotation frequency of the spinning tube for the SBM. Such robust tension measurement protocols were applied for Triton X-100 aqueous solutions at a fixed concentration above its critical micelle concentration (CMC). The EST value of the model solution was 31.5 ± 0.1 mN·m^{-1} with the EBM and 30.8 ± 0.2 mN·m^{-1} with the SBM. These protocols provide robust criteria for establishing the EST values.

Second, the EIFTs of a commercial single chain anionic surfactant solution in a synthetic brine against a crude oil from an active reservoir were determined with the new protocol described earlier. The commercial surfactant used here has an oligopropoxy group between a hydrophobic chain and a sulfate head group. The synthetic brine has 9,700 ppm of total dissolved salts, which are a mixture of sodium chloride (NaCl), potassium chloride (KCl), manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$), magnesium (II) chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), sodium bicarbonate ($NaHCO_3$), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$). The DSTs curves of the surfactant concentrations from 0.1 ppm to 10,000 ppm by weight had a simple adsorption/desorption equilibrium at air/water surface with surfactant diffusion from bulk aqueous phase. Such a mechanism was also observed from the tension relaxation behavior after area perturbations for the oil/water interfaces while DIFT measurements. The CMC of the commercial surfactant was determined to be 12 ppm in water and 1 ppm in the synthetic brine used. From the initial tension reduction curves from DST and DIFT measurements, the equilibrium timescales were shorter with brine than with water, because the adsorbed surfactant on the oil/water interfaces were partitioned into oil phases. For both DST and DIFT results suggest that the adsorbed surfactant layer at interfaces were typical adsorbed soluble monolayers.

Third, the phase and rheological behavior of a commercial anionic surfactant in water and in brine are important for large scale applications. A phase map of the surfactant at 25 °C at full range of surfactant concentration was obtained. The supramolecular structures of the various phases were characterized by dynamic light scattering (DLS), cryogenic transmission electron microscopy (cryo-TEM), conductimetry, densitometry, and x-ray scattering. The identified phases evolved as the surfactant concentration was increased; they were a micellar solution phase, a hexagonal liquid crystalline phase, and a lamellar liquid crystalline phase. In addition, the characterization results provided detailed information about supramolecular structure parameters such as micellar sizes and their aggregation numbers, and liquid crystal spacings. The phase and rheological behavior trends identified here were of great importance because the trend was similar to that of single chain monoisomeric surfactant. Thus, this study provides a potential universality of phase behavior trends of surfactant-water systems despite of the multicomponent nature of surfactants.

Fourth, the EIFTs of the pre-equilibrated mixtures of surfactant, brine, and oil were determined and compared to the EIFTs prior to pre-equilibration, in order to systematically identify the most relevant IFT for oil recovery. The EIFT between surfactant solutions and oil without any pre-equilibration prior to tension measurements is defined as the un-pre-equilibrated EIFT ($EIFT_{up}$). The EIFT between oil and water phases after the pre-equilibration of surfactant, brine, and oil is defined as pre-equilibrated EIFT ($EIFT_p$). The $EIFT_p$'s were generally higher than $EIFT_{up}$'s. In addition, the effects of three mixing methods and the water-to-oil volume ratio (WOR) on the $EIFT_p$ were evaluated. Out of three mixing methods, (A) mild mixing, (B) magnetic stirring, and (C) shaking vigorously by hand, method C produced mixtures which are the closest to the equilibrium state. The mixtures produced by method C had the largest decrease of the surfactant concentration during pre-equilibration due to the surfactant partitioning into oil phases. Moreover, the WOR affects the $EIFT_p$ significantly due to the preferential partitioning of surfactant components into oil phases. More specifically, the WOR and the $EIFT_p$ were found to be inversely correlated, because the amount of partitioned surfactant increased as the oil volume fraction increased. The $EIFT_p$'s were different from the $EIFT_{up}$'s at the same total surfactant concentrations in the aqueous layer evidently because of preferential partitioning of the various surfactant components.

Finally, the effect of surfactant losses due to adsorption into the rock surface on the pre-equilibrated EIFT ($EIFT_p$) were evaluated to improve surfactant formulation protocols. Here, five types of EIFTs were identified, along with robust protocols for determining them. These are: (I) the un-pre-equilibrated equilibrium IFT ($EIFT_{up}$); (II) the un-pre-equilibrated EIFTs in the presence of rock ($EIFT_{up,rock}$); (III) the pre-equilibrated EIFTs ($EIFT_p$) in the presence of oil; (IV) the pre-equilibrated EIFT in the presence of rock and oil ($EIFT_{p,rock}$); and (V) the effluent EIFT ($EIFT_{eff}$). The $EIFT_{up}$ is the EIFT of the aqueous surfactant/brine solution against an oil drop without any pre-equilibration. The $EIFT_{up,rock}$ is the EIFT between an oil drop and the surfactant solution after pre-equilibration with a rock sample to account for adsorption losses. The $EIFT_p$ is the EIFT between the pre-equilibrated water and the oil phases from surfactant/brine/oil mixtures. The $EIFT_{p,rock}$ is the EIFT between the pre-equilibrated water and the oil phases from surfactant/brine/oil/rock mixtures. The $EIFT_{eff}$ is the EIFT from an effluent sample mixture of a laboratory-scale core flood test. Among the five types of EIFTs, the $EIFT_{p,rock}$ was found to be the most important for the highest oil recovery performance in core flood tests, because it captures the most important surfactant partition processes, the partitioning to the oil phase and the partitioning by adsorption on the rock surface. Among three surfactant formulations tested with core flood experiments, the one with the lowest $EIFT_{p,rock}$ (~0.01 $mN \cdot m^{-1}$) had the highest oil recovery ratio (78%), and the one with the highest $EIFT_{p,rock}$ (~0.2 $mN \cdot m^{-1}$) had the lowest oil recovery ratio (55%). The other EIFTs correlated less with the oil recovery performance. Identifying surfactant formulations that have low or ultralow EIFTs, especially ultralow $EIFT_{p,rock}$'s, are critical for screening formulations appropriate for core flood tests and target field applications, and for predicting oil recovery performance. These works are a significant contribution for improving (a) the surfactant formulation evaluation protocols, and (b) the utilization of reliable IFTs and phase behavior test protocols for oil recovery and many other surfactant and colloid sciences applications.