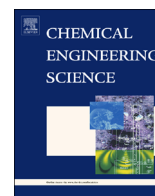




ELSEVIER

Contents lists available at ScienceDirect

## Chemical Engineering Science

journal homepage: [www.elsevier.com/locate/ces](http://www.elsevier.com/locate/ces)

# Systematic study of the effect of electrolyte composition on interfacial tensions between surfactant solutions and crude oils



Thomas Tichelkamp\*, Erlend Teigen, Meysam Nourani, Gisle Øye\*

Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælandsvei 4, NO-7491 Trondheim, Norway

## HIGHLIGHTS

- IFT measurements between crude oils and AOT solutions at low ionic strength.
- Equilibrium and dynamic IFT strongly dependent on bivalent/monovalent ratio.
- Minor change of bivalent/monovalent ratio alters IFT by one order of magnitude.
- Alkaline earth ions important to consider in low salinity EOR processes.

## ARTICLE INFO

### Article history:

Received 20 January 2015

Received in revised form

13 April 2015

Accepted 17 April 2015

Available online 29 April 2015

### Keywords:

Surfactant  
Interfacial tension  
Petroleum  
Low salinity  
EOR  
Calcium ions

## ABSTRACT

Dynamic and equilibrium interfacial tensions (IFT) were measured between four crude oils and aqueous low salinity solutions of the anionic surfactant AOT with different molar ratios between calcium and sodium ions. The ion strength of the electrolyte was kept constant at 20 mmol/L for all experiments. Slight changes of the calcium/sodium ratio altered the equilibrium oil/water IFT by more than one order of magnitude in the presence of surfactant. Experiments, in which either AOT was excluded or crude oil was replaced by pure hydrocarbons, were conducted in order to determine the relative impact of surfactant–electrolyte and crude oil–electrolyte interactions. In the presence of calcium, AOT dominated the interfacial properties. In sodium brine synergistic effects of AOT and surface active oil components on IFT were observed.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Surfactant flooding has for many decades been a promising method for mobilizing residual oil from mature reservoirs. The incremental recovery depends strongly on the capillary number ( $N_c$ ), which is reversely proportional to the IFT between the reservoir fluids (Butt et al., 2008). Fulcher et al. (1985) showed that an increase of capillary number by two or three orders of magnitude can decrease the residual oil saturation of a reservoir by tens of percent.

Anionic surfactants have been applied in sandstone reservoirs at so called “optimal salinity” to gain ultralow IFT values and low viscous “Winsor III” microemulsions, (Salager et al., 2013) in which large amounts of oil are dissolved per volume of water and surfactant. Even though the properties of Winsor III microemulsions

seem ideal for enhanced oil recovery, some drawbacks and possible complications can be related to the physics and chemistry of the systems. Winsor III behavior occurs at conditions where the solubility of the surfactant is equal in both oil and water and the high interfacial activity leads to increased surfactant adsorption to rock surfaces (Johannessen and Spildo, 2013; Spildo et al., 2014). This results in a considerable loss of surfactant in the reservoir and reduced EOR efficiency. As the Winsor III region is relatively narrow, slight changes in salinity, pH or temperature in the reservoir can lead to a “Winsor II” phase behavior and formation of highly viscous and less mobile water-in-oil microemulsion as well as surfactant loss due to phase trapping (Holmberg et al., 2002; Alagic and Skauge, 2010).

In recent years high EOR potential by changing rock wettability and reducing residual oil saturation has been shown for low salinity (LS) water flooding (Hill and Milburn, 1956; McGuire et al., 2005; Farooq, 2011; Ashraf et al., 2010; Tang and Morrow, 1997; Secombe et al., 2008, 2010). Furthermore, surfactant flooding with LS surfactant slugs and surfactant flooding in pre-established LS environments have become a separate and

\* Corresponding authors.

E-mail addresses: [thomas.tichelkamp@ntnu.no](mailto:thomas.tichelkamp@ntnu.no) (T. Tichelkamp), [gisle.oye@chemeng.ntnu.no](mailto:gisle.oye@chemeng.ntnu.no) (G. Øye).

promising area of research (Alagic and Skauge, 2010; Alagic et al., 2011; Johannessen and Spildo, 2013; Spildo et al., 2012).

Spildo et al. (2014) suggested that surfactant flooding at “sub-optimal salinity”, giving oil-in-water (Winsor I) microemulsions, can provide high oil solubilization and much lower surfactant retention than in Winsor III systems. In addition, these conditions were more stable to salinity and temperature changes. Further adsorption/desorption studies have shown that reduced salinity can reduce surfactant adsorption to polar mineral surfaces and increase water wetness of the surfaces by desorption of polar oil components (Helsing and Rennie, 2010; Nourani et al., 2014).

Previously a lot of work has been done on describing systems containing hydrocarbons, brine and surfactant. The interfacial activity of ionic surfactants, and consequently the phase behavior of the system, is known to depend strongly on salinity, temperature and ion valence (Sein et al., 1993, 1996; Sein and Engberts, 1995; Aveyard et al., 1985, 1986; Tichelkamp et al., 2014).

However, in petroleum science salinities are commonly declared as the gravimetric value TDS (total dissolved solid) in units of ppm, not considering the high abundance of alkaline earth ions and different types of anions in formation and injection water.

The aim of this work was to study how the IFT between crude oils and brines containing dissolved surfactants was affected when the ratio between bivalent and monovalent ions was systematically changed, while the ionic strength of the brines was kept constant.

In order to determine which effects were due to surfactant–electrolyte interactions and which effects were related to chemical or physical properties of the crude oils, IFT of a) crude oil/brine+surfactant; b) crude oil/brine (pH=6 and pH=11) and c) hydrocarbon/brine+surfactant were studied.

## 2. Material and methods

### 2.1. Chemicals

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 96%; Fig. 1) and toluene (AnalaR NORMAPUR<sup>®</sup>, ≥ 99%) were provided by VWR International AS. Dodecane (Reagent Plus<sup>®</sup>, ≥ 99%) and Calcium chloride dihydrate (p.a., ≥ 99%) were provided by Sigma-Aldrich Corporation and Sodium chloride (p.a., ≥ 99.5%) by Merck KGaA. All chemicals were used as received.

### 2.2. Aqueous solutions

Surfactant solution (4.94 mmol/L AOT) and different brines with ionic strength of 40 mmol/L were mixed 1:1 to give solutions of 2.47 mmol/L AOT and an ionic strength of 20 mmol/L for the background electrolyte. The brines were prepared with different molar ratios between sodium and calcium ions, referred to as  $X_{Ca/Na}$  [mol/mol]. The pH was adjusted by addition of 1M sodium hydroxide solution.

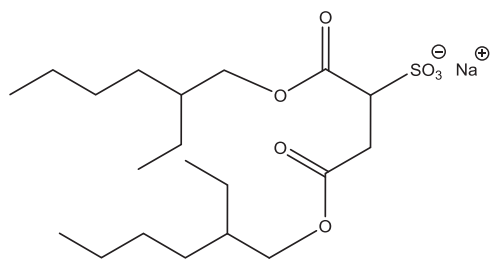


Fig. 1. Chemical structure of Sodium bis(2-ethylhexyl) sulfosuccinate.

### 2.3. Oils

Four stock tank crude oils from the Norwegian Continental Shelf and Germany, with a span of chemical and physical properties (Table 1), were used as received. Dodecane and 90:10 (v:v) mixtures of dodecane and toluene were used as model oils in some of the measurements.

### 2.4. Interfacial tension measurement

All experiments were performed at 60 °C in order to approach reservoir temperature. IFT was measured using a Spinning Drop Video Tensiometer (SVT20) from DataPhysics Instruments GmbH, Germany. Supporting information about the spinning drop technique is found in Refs. (Vonnegut, 1942; Manning and Scriven, 1977; Puig et al., 1992; Hu and Joseph, 1994; Viades-Trejo and Gracia-Fadrique, 2007). The aqueous phase was pre-heated to 60 °C and carefully injected into the glass tube. The capillary was tilted upside down, and a drop of the respective oil phase was injected with a syringe before the capillary was closed with a screw on lid with PTFE septum. The rotation speed was chosen so that the bubble had an elliptical shape and showed no tendency to split up into smaller droplets. The SVTS 20 IFT software (default software package of SVT20) was used to determine IFT as a function of the bubble profile, according to the method of Cayias, Schechter, and Wade (CSW).

The reported IFT values were average values from the IFT/time curve after reaching the specific equilibration time.

### 2.5. Extraction of water soluble crude oil compounds into brines

50 mL brine and 5 mL crude oil were filled into 50 mL Schott bottles and shaken for 8 h. The oil phase was thereafter removed by centrifugation (2 × 30 min at 11000 rpm). Surface tensions of the aqueous phases were measured with the DuNoüy ring method, using a Sigma 70 Tensiometer (KSV Instruments Ltd., Finland).

UV–vis spectra of the solutions, with mQ water as baseline, were measured using a UV-2401PC (Shimadzu Corporation). If the absorbance at 280 nm (aromatic hydrocarbons) exceeded a value of 1, the sample was diluted with mQ water.

## 3. Results and discussion

### 3.1. Crude oil/brine+surfactant

Fig. 2 shows the evolution of IFT with time for crude oil A and brines with different  $X_{Ca/Na}$ . The sample with pure sodium brine is shown separately because of the different time scale of equilibration. All crude oils followed qualitatively the same dynamic trend.

For the sample without calcium, and those with low calcium/sodium ratios, IFT changed in a non-monotonic manner before it subsequently leveled out in a region where it was stable for several hours.

Table 1

Viscosity, density (at 60 °C) and total acid number (TAN) of crude A, B, C and D (Full table of properties published in Ref. Tichelkamp et al., (2014)).

Crude oil	$\eta_{60\text{ °C}}$ (mPa s)	$\rho_{60\text{ °C}}$ (g/cm <sup>3</sup> )	TAN (mg KOH/g)
A	4.07	0.83	1.08
B	3.48	0.82	< 0.1
C	23.1	0.86	2.46
D	1.52	0.77	< 0.1

Download English Version:

<https://daneshyari.com/en/article/154680>

Download Persian Version:

<https://daneshyari.com/article/154680>

[Daneshyari.com](https://daneshyari.com)