

## **CRUDE OIL/BRINE INTERFACIAL TENSIONS**

Jill S. Buckley and Tianguang Fan  
PRRC, New Mexico Tech, Socorro, NM, USA

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### **ABSTRACT**

Interfacial tension (IFT) between crude oil and brine is an important variable in water/oil and water/oil/gas displacements. IFT influences capillary pressure, capillary number, adhesion tension, and the dimensionless time for imbibition. Despite its importance, there is little data available and even less data that can be related to key crude oil chemical properties such as acid and base number.

In this paper we present the results of a study of interfacial tensions for 41 well-characterized stock-tank crude oil samples. Transient IFTs measured by the pendant drop technique were monitored as a function of time. The effects of salinity and pH (over the range from 3 to 10) have been investigated and correlations observed between IFT and an oil's acid number, base number, and amount of asphaltenes. This extensive data set will be of use to core analysts when they compare capillary pressures measured with different fluid pairs or design core floods with model fluids, and in many other applications. It can also be used to examine mechanistic explanations for the magnitude of IFT between a crude oil and brine.

### **INTRODUCTION**

IFT values between crude oil and aqueous solutions are time dependent. This may be due in part to slow diffusion of some components across the interface, however changes with time are not eliminated by pre-equilibration of the oleic and aqueous phases [1]. Molecular rearrangement at the interface may also contribute to IFT values that change with interface age. Reactions of the acidic and basic functional groups of heavier crude oil components can occur when the aqueous phase pH is very high or very low, generating in-situ surfactants that can further alter the IFT as a function of time. Donaldson et al. [2] reported IFT values for 43 crude oils and 0.1M NaCl that range from a low of 9.9 to a high of 31.5 mN/m.

Ball et al. [3] proposed a classification of IFT measurements based on changes in the oil to aqueous phase mass ratio and interfacial area during the measurement. If both mass ratio and interfacial area are constant (e.g., du Nouy ring and Wilhelmy plate measurements) the method is static. Static methods produce a single value of IFT. If both mass ratio and interfacial area are changing (e.g., drop volume measurements) the method is dynamic. For systems with IFT changing with time, the results of such measurements can depend on the rate of drop formation [4]. In methods that are referred to as transient, the mass ratio is set at the beginning of an experiment and changes in

interfacial area are monitored as a function of interfacial age. In this work, we use the pendant drop method to measure transient IFT between crude oils and a selection of aqueous phases.

We have collected oil samples from around the world; their physical, chemical, and surface properties are collected in our Crude Oil-Wettability (CO-Wet) database [5,6]. For this IFT study, we have selected oils with a wide range of properties in order to determine whether any of the properties we measure or their combinations are predictive of IFT.

## **EXPERIMENTAL MATERIALS AND METHODS**

### **Fluids**

#### Crude Oil Samples

41 oil samples were selected from the population of the CO-Wet database [5,6]. Five are heavy oils (API gravity  $< 22.3^\circ$ ), 22 are medium gravity and the remaining 14 are light oils (API gravity  $> 31.1^\circ$ ). Oil properties routinely measured for these samples include density and viscosity as a function of temperature, average molecular weight, SARA fractions, refractive index, asphaltene stability conditions, isoelectric points, and wetting of mica under stable and unstable water film conditions. Correlations were tested between all available oil characterization data and resulting IFTs, although only the data giving the best correlations (amount of n-C<sub>7</sub> asphaltenes, acid number, base number and viscosity) and API gravity are included in this paper (see Appendix). Measurement techniques have been described previously [5,6]. The samples range in amount of n-C<sub>7</sub> asphaltenes from a low of 0.05% to a high of 8.75%; acid numbers range from the limit of detection (about 0.01 mg KOH/g oil) to a high of 3.92 mg KOH/g oil; base numbers are from 0.11 to 5.19 mg KOH/g oil; viscosities are in the range 1.2 to 661 cP at 20°C. Although not shown here, similar correlations would be obtained if the amounts of n-C<sub>6</sub> asphaltenes were substituted for the n-C<sub>7</sub> values.

#### Aqueous Phase

Several aqueous phase compositions were tested including double-distilled water (DDW), 0.1M NaCl, and synthetic sea water (SSW). The pH of the distilled water and sodium chloride solutions was adjusted by addition of small amounts of HCl or NaOH. pH measurements were made immediately before the solutions were used in IFT tests since pH of unbuffered solutions can change with time.

A pH meter (Orion Model 520A) equipped with a combination pH electrode (Corning) was used to measure pH.

### **Transient IFT Measurement**

IFT was measured as a function of drop age using a Data Physics OCA20 pendant drop apparatus with SCA20 software. IFT was calculated from drop shape by fitting to the Young-Laplace equation.

The pendant drop method of IFT measurement requires that a stable drop be formed. At tensions less than about 1 mN/m, oil streams continuously out of even the smallest available drop-forming needle. Accurate measurements can be made by other methods, such as the spinning drop technique [7], but such observations were beyond the scope of the present study.

#### Measurement Protocol and Modeling of IFT vs. Time

Preliminary studies showed that if drop volumes were less than about 6  $\mu\text{l}$ , IFT values were lower than measurements using larger drop volumes. Drops varying in volume from about 7 to 30  $\mu\text{l}$  gave identical results.

For the following studies of crude oil IFT, a needle with OD of 0.7 mm was used to form a 10  $\mu\text{l}$  drop. Drop formation time was two seconds. Data recording began immediately after drop volume reached 10  $\mu\text{l}$  and continued for 2000 s (about 33 min). A summary of the oil/aqueous phase combinations tested is included in the Appendix.

A model equation for IFT vs. time of asphaltene solutions has been proposed [8], based on similar phenomena of rapid diffusion to an interface, followed by slow rearrangement reported for proteins. The data were fit to an equation of the form:

$$\gamma = \gamma_{eq} + (\gamma_o - \gamma_{eq}) * e^{-t/\tau} \quad (1)$$

where  $\gamma$  is interfacial tension (mN/m) with subscripts eq=equilibrium, and o=zero time or initial, t is time,  $\tau$  is a characteristic time constant with the same units as time, t.

#### Statistical Analysis

Statistical correlations were tested in Microsoft Excel using Analyze-It version 1.62 (Analyze-It Software, Ltd.).

## **RESULTS AND DISCUSSION**

### **IFT as a Function of Time**

A typical IFT measurement is shown in Fig. 1 for crude oil E-1XCO-01 and SSW. The change in IFT from formation of a new drop to a drop age of 2000 s is 2.9 mN/m and the final IFT is 21.2 mN/m. The data were fit to Eq. 1 using a time constant  $\tau$  of 140 s.

Detailed results of 260 tests were reported by Fan and Buckley [9]. The average decrease in IFT from initial to equilibrium conditions was  $4.7 \pm 2.9$  mN/m (or about 23% of initial IFT values) with larger changes occurring mainly in the higher pH measurements. The

largest change observed over the 2000 s period was 15.6 mN/m for crude oil C-Br-01 measured in 0.1M NaCl with pH adjusted to 9.

### **IFT Measurements for Many Crude Oil-Brine Combinations**

Linear multivariate statistical analysis of the final or equilibrium IFT data for all the oil/aqueous phase combinations shown in the Appendix produces the correlation shown in Fig. 2. All of the correlations shown in this paper are for the equilibrium IFT values although initial values and time constants were also tested. Many crude oil properties accumulated in the CO-Wet database were examined. Density, refractive index, amounts of saturates, aromatics, and resins, and iso-electric points showed no significant correlation with IFT. The pH of the brine influences IFT, as expected from earlier work [10] and reports in the literature [11,12]. In addition, the amount of n-C<sub>7</sub> asphaltene, acid and base numbers, and viscosity all appear to be correlated with IFT. Oil viscosity at 20°C was a significant variable only in combination with acid number. If acid number was omitted, viscosity no longer contributed to the correlation. Tests of oil property correlations among 139 oil samples in the CO-Wet database show that the log of viscosity at 20°C is highly correlated to a group of properties that include base number, amount of n-C<sub>7</sub> asphaltene, API gravity (or density) and average molecular weight. No relationship between acid number (or any of the other variables in the database) and viscosity could be discerned.

There is too much scatter for such a relationship to be used to predict IFT from oil properties, but it is instructive with regard to differentiating the oil properties that influence the equilibrium values of transient IFT at oil/water interfaces. The probability (p) of even the least significant variable (viscosity) not being correlated with IFT is less than 0.023, showing that all the variables listed are significant. Increasing amount of n-C<sub>7</sub> asphaltene, higher base number and higher viscosity correspond to higher IFT with brine of a given pH. The correlation with pH is negative because large decreases in IFT can occur at the highest pHs tested in this study. IFT can also decrease at low pH, but over the range studied, this effect was much smaller. Increasing acid number contributed to a decrease in IFT. As might be expected, correlation coefficients are low for any one variable with the highest being n-C<sub>7</sub> asphaltene amount ( $R^2 = 0.23$ ) and the acid number the lowest ( $R^2 = 0.01$ ). Better correlations can be obtained by separating the data into different aqueous phase pH and composition ranges and focusing on the effect of oil properties.

### **Effect of pH of 0.1M NaCl Aqueous Phase**

#### Comparison of Low and High Acid Number Oils

The effect of pH on IFT was investigated for two suites of oils, selected from those with the lowest and highest acid numbers, as shown in Fig. 3. If the results near pH 6 are compared, both sets span most of the range from about 10 to 30 mN/m, but the response to changes in pH away from pH 6 are somewhat different. (Note that cases where tension was too low to form a stable drop are shown as going to zero although the phases are still

immiscible and low tensions would be measurable by other methods.) Two of the low-acid-number samples have IFTs that decrease continuously with increasing pH and four have measurable IFTs at the highest pH tested (about 11). All of the high-acid-number oils exhibit a plateau or a maximum IFT value at low to intermediate pH; IFTs are all below the measurable level in the highest pH tests. No distinctions were found between high acid number oils with low base numbers compared to those with high base numbers. IFT would likely decrease if pH were reduced to values less than a pH of 3, but these extremely acidic conditions were not included in this series of tests.

#### IFT with Different Oils at Constant pH—Correlation with Oil Properties

The IFT data were divided into groups with constant brine composition (DDW, 0.1M NaCl, and SSW) and pH ( $\pm 0.5$  pH unit). The data were tested for single and multivariate linear correlations with all of the information stored in the CO-Wet database. A set of correlating variables (n-C<sub>7</sub> asphaltene amount, acid and base numbers, and viscosity) was selected on the basis of these preliminary tests. Each group was tested with the full set of variables and those with p-values (the probability that a variable has been included in error) greater than 0.05 were eliminated. The results of the statistical tests, summarized in Table 1 and plotted in Fig. 4 for the 0.1M NaCl solutions, show that the weight percent of n-C<sub>7</sub>asphaltenes correlates positively with IFTs in all three pH groups (pH 3, 6, and 9). In other words, oils with larger amounts of asphaltenes have higher IFTs, with the greatest effect evident at pH 6. Note that asphaltenes do not behave as surfactants, i.e., they do not lower oil/water IFT. At acidic conditions, IFTs are lower for oils with higher acid numbers, but this effect is offset somewhat by a small positive correlation with viscosity. At pH 6, IFT increases with base number. The same is true at pH 9, but IFTs are generally lower, as shown by the reduced value of the intercept. Similar results were obtained for the DDW data, but the correlations were more scattered. No clear correlation was obtained between IFT of oil in SSW and any set of oil properties.

**Table 1. Best correlations with oil properties for IFTs at constant pH**

pH	n	R <sup>2</sup>	intercept	coefficients		
				n-C <sub>7</sub> asph wt%	Acid # (mg KOH/g oil)	Base # viscosity at 20°C (cP)
3	17	0.74	16.8	0.598	-1.297	0.014
6	20	0.70	11.6	1.243		1.691
9	15	0.56	6.3	1.165		2.576

#### **Synthetic Sea Water**

Synthetic sea water contains divalent calcium and magnesium cations that may have specific interactions with ionizable species at the oil/water interface. Nevertheless there does appear to be some correlation between equilibrium IFT measured in DDW (pH 6) and measurements with the same oils and SSW, as shown in Fig. 5. Only a few direct comparisons are available for 0.1M NaCl (pH 6) and SSW measurements, but they also appear to be related.

### Identification of Contaminated Samples

Identification of samples that may be contaminated with a wide variety of drilling and oil-field chemicals, many of which are surface active, is important for making valid laboratory measurements. Hirasaki and Zhang [13] suggested that oils with low IFTs that change with time may be contaminated, but no quantitative limits were suggested. Examination of the data in this study shows a wide range of IFTs that depend on aqueous phase composition as well as that of the oil. Some guidance is needed to pick out contaminated samples based on low IFT or transient effects. We calculated the change in IFT from  $\gamma_o$  to  $\gamma_{eq}$  (after 2000 s) for the pH 3, 6, and 9 data. The results ( $\gamma_o - \gamma_{eq}$ ) could be expressed in mN/m, but that might be misleading for samples with low  $\gamma_o$  values. Instead the frequency distribution is shown as a fraction of  $\gamma_o$  in Fig. 6. At pH 3, all of the fractional decreases  $[(\gamma_o - \gamma_{eq})/\gamma_o]$  are less than 0.4. At pH 6, most of the results are still in that range, but several oils decrease more than that, with the highest being those for the contaminated oil MY1-02. At pH 9, it is not possible to ascribe transient IFT exclusively to contamination.

It is also possible to test for contamination by comparing measured IFT to the IFT predicted from the correlations with crude oil properties. Figure 7 shows two examples of oils that clearly do not fit the established correlation for IFT in 0.1M NaCl at pH 6. One of these samples is MY1-02, previously identified as contaminated [13]. The other sample was received very recently, after completion of the correlation study. Both have IFTs that are much lower than would be predicted on the basis of their chemical properties. The correlation method can be used in addition to observations of transient IFT to help distinguish cases where IFT is low because of contamination from those where IFT is expected to be low due to characteristics of the crude oil/brine combination.

### CONCLUSIONS

- IFT of crude oils varies predictably with pH and composition of the aqueous phase. Key oil properties that correlate with IFTs measured with pH-adjusted distilled water and 0.1M NaCl solutions are the amount of n-C<sub>7</sub> asphaltenes, acid number, base number, and viscosity. Different combinations of these variables dominate in acidic, near-neutral, weakly basic, and high pH ranges.
- Amount of asphaltenes, as measured by precipitation with n-heptane, is an important parameter at all conditions. IFT increases with increasing amount of asphaltene. Asphaltenes are not comparable to surfactants that lower IFT.
- Acid number and viscosity mainly affect IFT at acidic conditions. IFT decreases with higher acid number and increases with higher viscosity. Base number affects IFT at near-neutral and weakly basic conditions. IFT increases with increasing base number. Acid number is important in the very basic range above pH 10. Ultralow tensions are achieved only if acid numbers exceed 0.1 mg KOH/g oil.
- The IFT trends established in this work for a wide range of crude oils can be used to help identify oil samples that may be contaminated with surface-active oilfield chemicals.

## ACKNOWLEDGEMENTS

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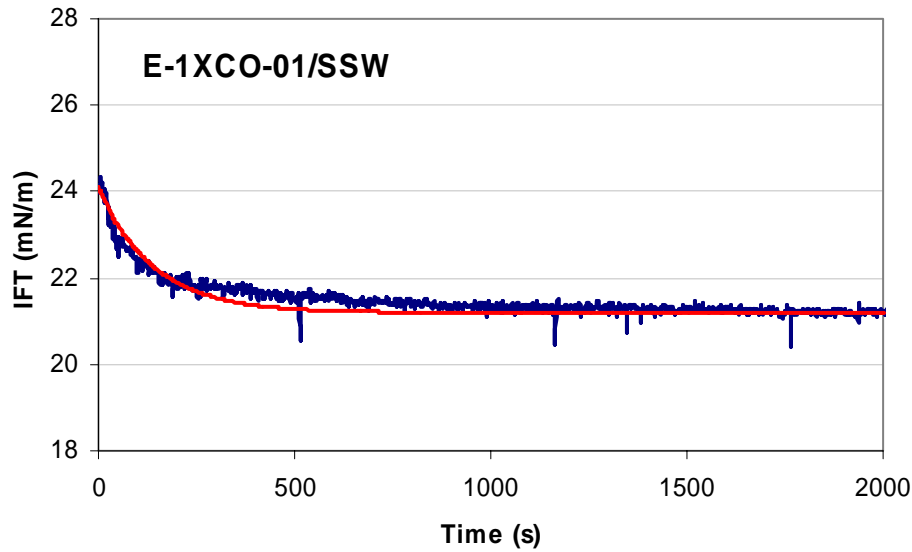


Figure 1. IFT vs. time for crude oil E-1XCO-01 and SSW. The data are fit by the smooth line, which has the following parameters in Eq. 1:  $\gamma_0 = 24.1$  mN/m,  $\gamma_{eq} = 21.2$  mN/m,  $\tau = 140$  s.

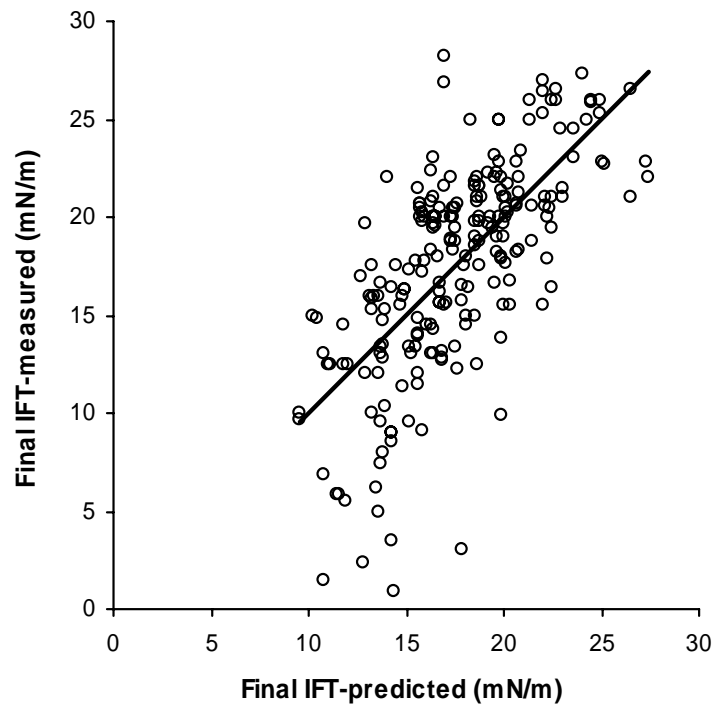
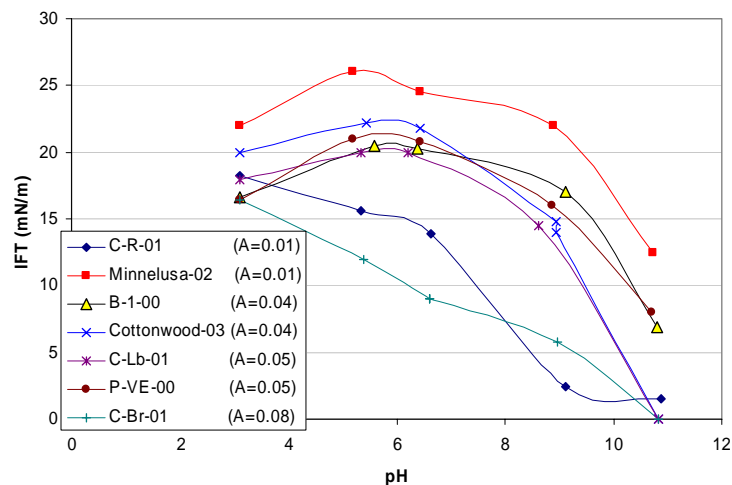
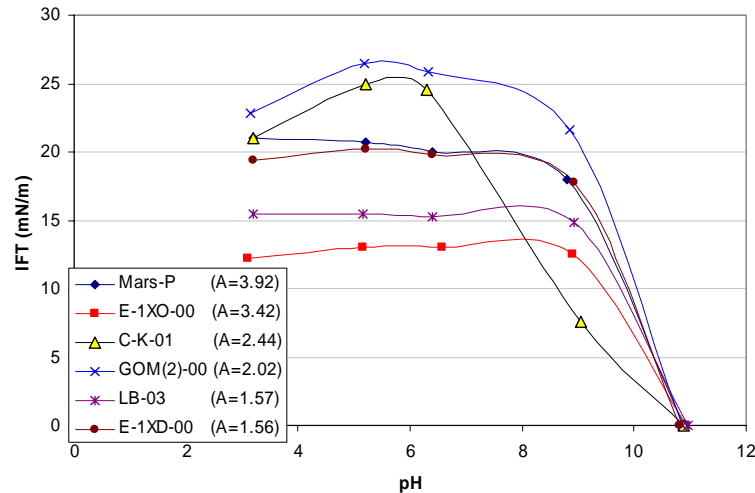


Figure 2. Equilibrium IFT values correlate with pH of the aqueous phase, the amount of n-C7 asphaltene (As), acid number (A), base number (B), and viscosity ( $\mu$ ) of each oil. Equation of the correlating line is  $\gamma_{eq} = 21.7 - 1.14 \text{ pH} + 0.745 \text{ As} - 1.21 \text{ A} + 1.15 \text{ B} + 0.0073 \mu$  and  $R^2 = 0.46$ .



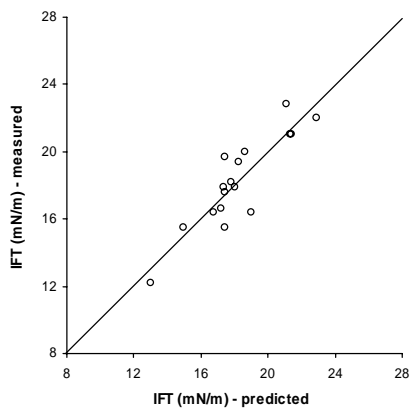


(a) low acid number oils

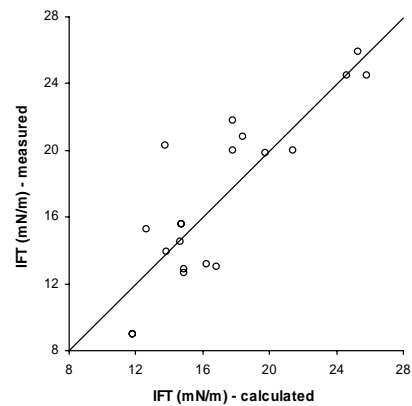


(b) high acid number oils

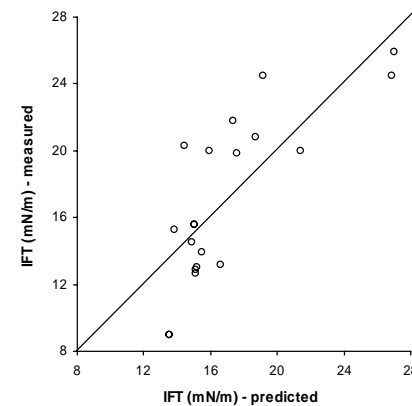
Figure 3. pH dependence of IFT for low and high acid number oils measured against pH-adjusted 0.1M NaCl.



(a) pH 3



(b) pH 6



(c) pH 9

Figure 4. Correlations of IFT for crude oils measured against pH-adjusted 0.1M NaCl with amount of n-C7 asphaltene, acid number, base number, and viscosity (see Table 1).

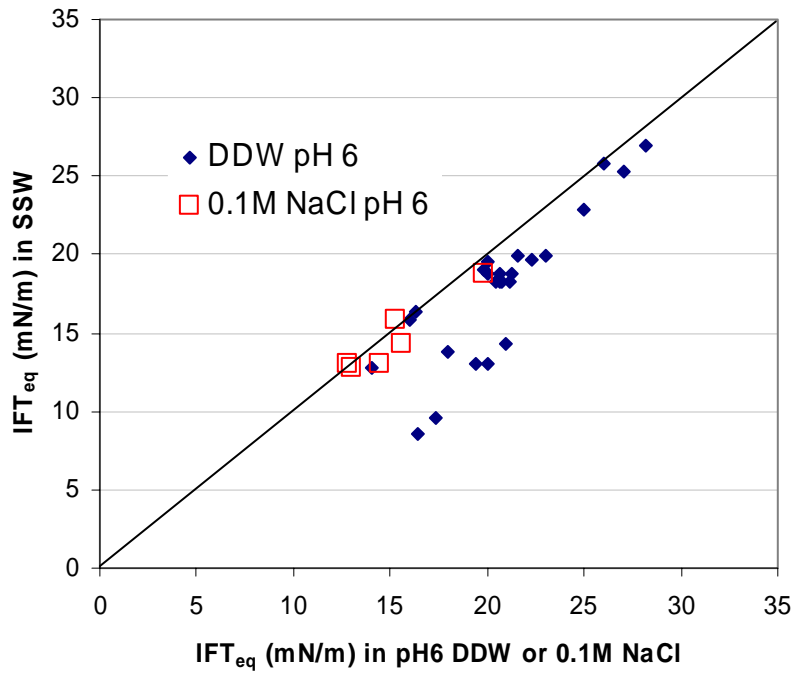


Figure 5. Relationships between IFT for oil vs. SSW the same oil vs pH 6 DDW or 0.1M NaCl.

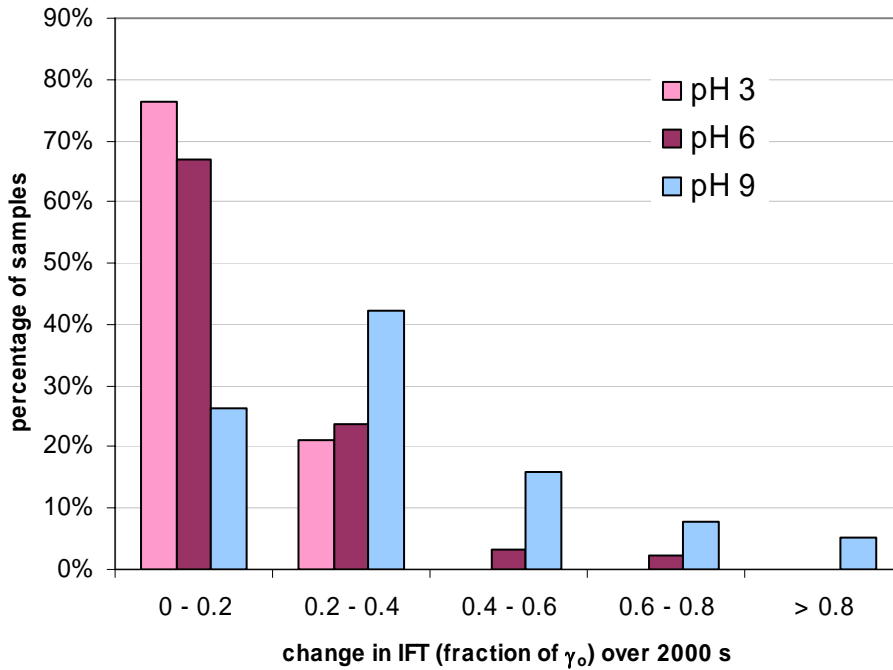
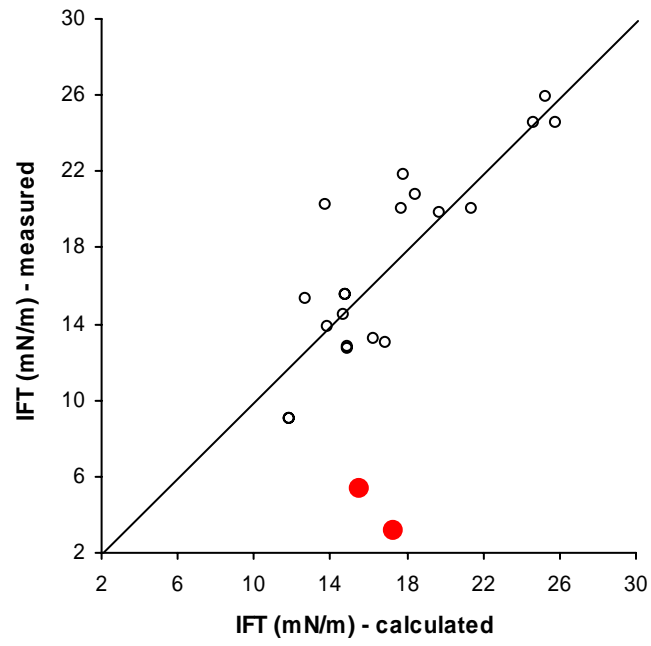


Figure 6. Frequency distribution of different values of  $(\gamma_o - \gamma_{eq}) / \gamma_o$  for IFTs measured between crude oils and aqueous phases with pH 3, 6 and 9. Measurements with contaminated sample MY1-02 can be distinguished at pH 6 because they are the only ones in the 0.6 to 0.8 range.



**Figure 7. Measured IFTs of contaminated oils fall far below those calculated based on their oil properties and correlation for 0.1M NaCl in Table 1.**

## Appendix

Table A1. Selected properties of crude oil samples and test summary

oil sample	API gravity (°)	n-C <sub>7</sub> asphaltenes (wt%)	acid	base	viscosity at 20°C (cP)	DDW pH:			0.1M NaCl pH:			SSW pH:
			number (mg KOH/g oil)	number		3	6	9	3	6	9	6
B-1-00	37.1	0.62	0.04	0.85	4.7	x	x	x	x	x	x	
C-A1-00	33.7	1.66	0.34	3.44	10.6		x					x
C-AG-03	40.3	0.14	0.08	0.50	1.9		x					x
C-AL-03	18.7	2.40	1.79	4.94	661.0		x					x
C-Br-01	48.0	0.05	0.08	0.11	1.2	x	x	x	x	x	x	
C-F2-03	27.9	1.97	0.70	1.32	28.6	x	x	x	x	x	x	
C-GC-T1-03	31.1	4.56	0.03	1.69	17.0		x					x
C-K-01	18.9	3.46	2.44	5.19	396.0	x	x	x	x	x	x	
C-Lb-01	31.7	1.60	0.05	2.50	22.6	x	x	x	x	x	x	
Cottonwood-03	26.4	2.51	0.04	1.87	26.1	x	x	x	x	x	x	
C-R-01	31.1	1.30	0.01	0.40	17.8	x	x	x	x	x	x	
C-T-02	34.2	1.36	0.01	1.30	9.4		x					x
E-1XCO-01	33.8	0.65	0.18	1.93	9.3		x					x
E-1XD-00	22.3	2.54	1.56	2.98	137.4	x	x	x	x	x	x	x
E-1XFR-01	40.0	0.26	0.16	0.65	3.7		x					x
E-1XO-00	21.9	0.76	3.42	2.57	15.3	x	x	x	x	x	x	x
E-2XR-00	25.4	1.33	0.91	2.46	47.0		x					x
E-8XFR-01	38.6	0.30	1.03	0.74	4.7		x					x
E-BL-00	31.3	3.58	0.17	1.33	23.4		x					x
E-S1XCA-01	23.2	2.08	0.48	3.42	80.6		x					x
E-S1XG-01	33.3	0.54	0.14	1.57	9.6		x					x
E-S1XL-01	33.5	0.42	0.48	1.83	10.3		x					x
E-S3XR-01	30	0.92	0.23	2.03	19.8		x					x
GOM(2)-00	21.2	8.63	2.02	1.79	122.3	x	x	x	x	x	x	
Gulfaks-96	27.1	0.40	0.24	1.19	15.8		x					
LB-03	30.6	0.07	1.57	0.59	13.1	x	x	x	x	x	x	x
Mars-P	16.5	4.77	3.92	2.30	481.0	x	x	x	x	x	x	
Minnelusa-02	24.3	8.75	0.01	2.01	60.5	x	x	x	x	x	x	
Minnelusa-03	24.5	7.20	0.12	1.71	58.1		x					x
MY1-02	27.0	1.59	0.50	1.17	27.7					c		
MY2-02	28.8	0.91	0.17	1.16	18.3	x	x	x	x	x	x	x
MY3-02	28.0	0.99	0.20	1.17	21.7	x	x	x	x	x	x	x
MY4-02	28.1	1.03	0.22	1.23	21.6	x	x	x	x	x	x	x
P-VE-00	30.6	3.43	0.05	1.54	16.3	x	x	x	x	x	x	
SQ-95	37.2	1.30	0.17	0.62	5.8	x	x	x				
S-Ven-39	28.8	5.79	0.14	1.68	29.8		x					x
S-Ven-40	30.2	6.08	0.13	1.62	23.7		x					x
S-Ven-41	28.7	7.17	0.43	1.78	33.7		x					x
Tensleep-99	31.1	4.10	0.10	1.03	18.7	x	x	x				
W-Br-03	32.7	0.41	0.12	1.56	12.3		x					x
W-Lo-03	28.1	1.68	0.39	0.94	17.8		x					
W-TH-05	31.8	2.78*	0.18	1.37	13.5					c		

c = contaminated oil sample, not included in correlations

\* n-C<sub>6</sub> asphaltenes