

WETTABILITY AND PREDICTION OF OIL RECOVERY FROM RESERVOIRS  
DEVELOPED WITH MODERN DRILLING AND COMPLETION FLUIDS

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## **Project Objectives**

The objectives of this project are:

1. to improve understanding of the wettability alteration of mixed-wet rocks that results from contact with the components of synthetic oil-based drilling and completion fluids formulated to meet the needs of arctic drilling;
2. to investigate cleaning methods to reverse the wettability alteration of mixed-wet cores caused by contact with these SBM components; and
3. to develop new approaches to restoration of wetting that will permit the use of cores drilled with SBM formulations for valid studies of reservoir properties.

## **Abstract**

Contamination of crude oils by surface-active agents from drilling fluids or other oil-field chemicals is more difficult to detect and quantify than bulk contamination with, for example, base fluids from oil-based muds. Bulk contamination can be detected by gas chromatography or other common analytical techniques, but surface-active contaminants can be influential at much lower concentrations that are more difficult to detect analytically, especially in the context of a mixture as complex as a crude oil.

In this report we present a baseline study of interfacial tensions of 39 well-characterized crude oil samples with aqueous phases that vary in pH and ionic composition. This extensive study will provide the basis for assessing the effects of surface-active contaminant on interfacial tension and other surface properties of crude oil/brine/rock ensembles.

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# Crude Oil IFT Measurements by the Pendant Drop Method

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## Introduction

Crude oils are complex mixtures of many thousands of components. We have collected oils from around the world and assembled information about their physical, chemical, and surface properties in our Crude Oil-Wettability (CO-Wet) database (Buckley, 2001; Buckley and Wang, 2002). The information stored in the database and the oil samples themselves represent a valuable resource that we use in this study to investigate the dependence of interfacial tension (IFT) on oil and aqueous phase compositions.

Crude oil/brine IFT measurements are challenging because of the complexity of oil and influence of brine compositions. Slow diffusion and reaction processes at the oil/brine interface make the IFT values time dependent. The chemical reactions of the acidic and basic functional groups in oil with the aqueous phase can generate in situ surfactants that can further alter the IFT.

IFT measurements can be static, transient, or dynamic depending on whether there are mass and surface area changes at the oil/brine interfaces with time (Ball et al., 1996). Examples of static measurements are du Nouy ring and stationary Wilhelmy plate methods, spinning and pendant drop methods are transient, and drop volume measurements are an example of a dynamic measurement method. The pendant drop method has been adopted in this work to track changes in IFT as a function of drop age for crude oils with varying acid and base numbers for a range of brine compositions.

## Experimental Methods

### *Fluids*

#### Aqueous phase composition

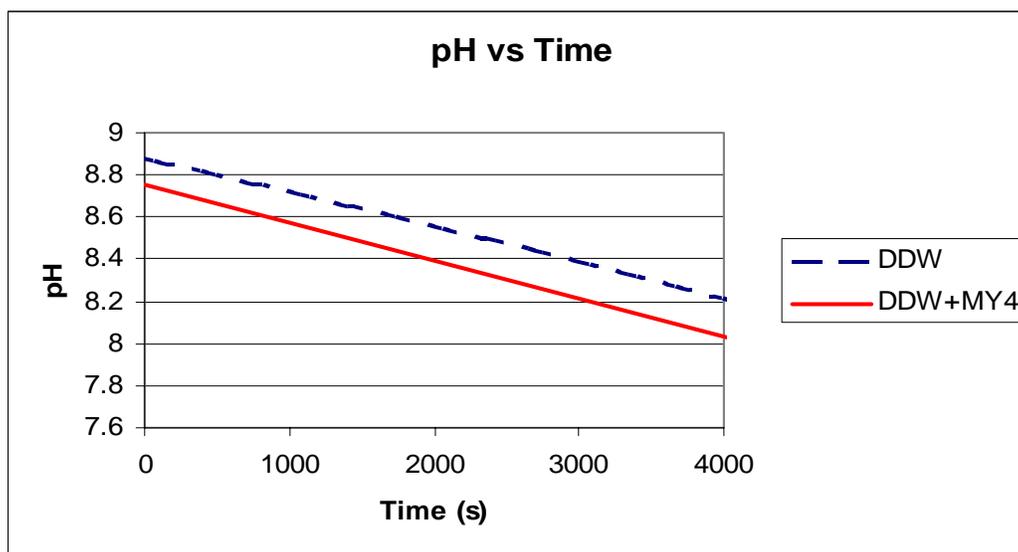
Aqueous phase compositions were based on one of three solutions: double-distilled water (DDW), 0.1M NaCl, or synthetic sea-water (SSW). The pH of DDW and 0.1M NaCl solutions were adjusted by addition of small amounts of HCl or NaOH. Two recipes were used for synthetic seawater, differing only in the presence or absence of sodium bicarbonate.

**Table 1. Composition of aqueous phase solutions**

	NaCl (mol/L)	CaCl <sub>2</sub> (mol/L)	MgCl <sub>2</sub> (mol/L)	Na <sub>2</sub> SO <sub>4</sub> (mol/L)	NaHCO <sub>3</sub> (mol/L)	pH adjusted with
DDW	0	0	0	0	0	HCl/NaOH
0.1M NaCl	0.100	0	0	0	0	HCl/NaOH
SSW	0.411	0.010	0.052	0.023	0	-
SSW-HCO <sub>3</sub>	0.411	0.010	0.052	0.023	0.005	-

pH drift with time

To avoid potential interference from buffer ions, the aqueous solutions used in this work were not buffered. Thus it was necessary to measure the value of pH immediately before each IFT test. It was found for solutions with pH less than 7, that pH was stable for more than two weeks. When the aqueous phase was at basic conditions, however, the pH was not stable even for a few hours. Figure 1 shows a typical rate of pH decrease for DDW (with pH adjusted by addition of NaOH) with and without a drop of crude oil present.



**Figure 1. pH of DDW, with pH adjusted to about 8.8 by addition of NaOH, decreases with time. The rate of decrease is similar for the pH adjusted DDW and for DDW plus a drop of MY4-02 crude oil. The amounts of oil and water reproduced the oil:water volume ratio in pendant drop experiments (about 1:400).**

Crude oil samples

A wide range of crude oil samples have been collected and characterized in previous studies of the effects on reservoir wetting of crude oils and their asphaltene components (Buckley, 2001, Buckley and Wang, 2002). Most previous studies of crude oil interfacial tensions focus on one or at most a few crude oil samples (e.g., Reisberg and Doscher, 1956; Freer et al. 2003). Given the complexity of crude oil composition, physically meaningful correlations to crude oil properties cannot be expected on the basis of studies of only a few samples.

### ***IFT measurement by pendant drop***

IFT was measured using a pendant drop apparatus from Data Physics (OCA 20 Contact Angle System). In this system, testing liquid in a gas-tight needle syringe was delivered by electronic control through a connecting tube and calibrated needle by using a stepper motor. The liquid dosing system had a delivery range of 0.1-5 $\mu$ l/s. The pendant drop image formed at the tip of needle can be captured digitally and then analyzed by the SCA 20 software (Dataphysics, 2003) and an interfaced computer. The high speed CCD video camera system can do dynamic tracking analysis at a speed of 1 image/s. The surface tension (SFT) or IFT was calculated by fitting the Laplace equation to the outline of the drop (Adamson and Gast, 1997) using the following equation:

$$\gamma = \Delta\rho * g * z / 2(H_A + H_B)$$

where  $\gamma$  is SFT or IFT (mN/m),  $\Delta\rho$  is density difference of two phases, and  $z$ ,  $H_A$ , and  $H_B$  are computer fitted image parameters. A thermal plate connected to a circulating water bath and an optical chamber can set at a desired temperature to an accuracy of  $\pm 0.5^\circ\text{C}$ . The densities of liquids were measured by a Mettler/PAAR DMA40 digital densitometer. In order to minimize the temperature error, the experiments were conducted at either  $20^\circ\text{C}$  or  $25^\circ\text{C}$ , close to the usual room temperature. The aqueous phase pH was measured with a combination Corning glass pH electrode with an Orion Model 520A pH meter. Some standard hydrocarbons were purified by passing through a silica-gel and alumina absorption column.

### ***Evaluation of the pendant drop apparatus***

#### Surface tension of water

The system at first was evaluated by measuring the SFT of double-distilled water (DDW) using an accessory needle (1.65 mm O.D.) from Dataphysics. From 10 different measurements, an average SFT value of 71.7 mN/m ( $25^\circ\text{C}$ ) was obtained with a usual calculation error less than 0.5% and standard deviation 0.7, while the SFT of water from the CRC handbook was reported to be 72.0 mN/m at the same temperature.

**Table 2. Selected properties of crude oil samples from CO-Wet database**

oil sample	n-C <sub>7</sub> asphaltenes (wt%)	acid number      base number		viscosity at 20°C (cP)
		(mg KOH/g oil)		
B-1-00	0.62	0.04	0.85	4.7
C-A1-00	1.66	0.34	3.44	10.6
C-AG-03	0.14	0.08	0.50	1.9
C-AL-03	2.40	1.79	4.94	661.0
C-Br-01	0.05	0.08	0.11	1.2
C-F2-03	1.97	0.70	1.32	28.6
C-GC-T1-03	4.56	0.03	1.69	17.0
C-K-01	3.46	2.44	5.19	396.0
C-Lb-01	1.60	0.05	2.50	22.6
Cottonwood-03	2.51	0.04	1.87	26.1
C-R-01	1.30	0.01	0.40	17.8
C-T-02	1.36	0.01	1.30	9.4
E-1XCO-01	0.65	0.18	1.93	9.3
E-1XD-00	2.54	1.56	2.98	137.4
E-1XFR-01	0.26	0.16	0.65	3.7
E-1XO-00	0.76	3.42	2.57	15.3
E-2XR-00	1.33	0.91	2.46	47.0
E-8XFR-01	0.30	1.03	0.74	4.7
E-BL-00	3.58	0.17	1.33	23.4
E-S1XCA-01	2.08	0.48	3.42	80.6
E-S1XG-01	0.54	0.14	1.57	9.6
E-S1XL-01	0.42	0.48	1.83	10.3
E-S3XR-01	0.92	0.23	2.03	19.8
GOM(2)-00	8.63	2.02	1.79	122.3
Gulfaks-96	0.40	0.24	1.19	15.8
LB-03	0.07	1.57	0.59	13.1
Mars-P	4.77	3.92	2.30	481.0
Minnelusa-02	8.75	0.01	2.01	60.5
Minnelusa-03	7.20	0.12	1.71	58.1
MY1-02	1.59	0.50	1.17	27.7
MY2-02	0.91	0.17	1.16	18.3
MY3-02	0.99	0.20	1.17	21.7
MY4-02	1.03	0.22	1.23	21.6
P-VE-00	3.43	0.05	1.54	16.3
SQ-95	1.30	0.17	0.62	5.8
S-Ven-39	5.79	0.14	1.68	29.8
S-Ven-40	6.08	0.13	1.62	23.7
S-Ven-41	7.17	0.43	1.78	33.7
Tensleep-99	4.10	0.10	1.03	18.7
W-Br-03	0.41	0.12	1.56	12.3
W-Lo-03	1.68	0.39	0.94	17.8

### IFT of decane in DDW

The IFT of decane (Fisher Chemicals, 99.8%) in double-distilled water (DDW) was measured at 20°C; the data are shown in Fig. 2. The IFT at zero time (IFT(0)) started at 52.3 mN/m and then slowly decreased to an equilibrium value (IFT(eq)) of 50.3 mN/m at the drop age of 2000 second. The reference IFT(0) value for decane in water at 20°C is 52.3 mN/m (Dataphysics) or higher (53.3 mN/m was reported by Goebel and Lunkenheimer, 1997). The decrease of IFT from 52.3mN/m to 50.3 mN/m indicates that there was a small amount of surface-active materials in this sample. One of the strengths of the pendant drop measurement technique is that changes with time can be recorded, helping to identify contaminated and/or reactive samples.

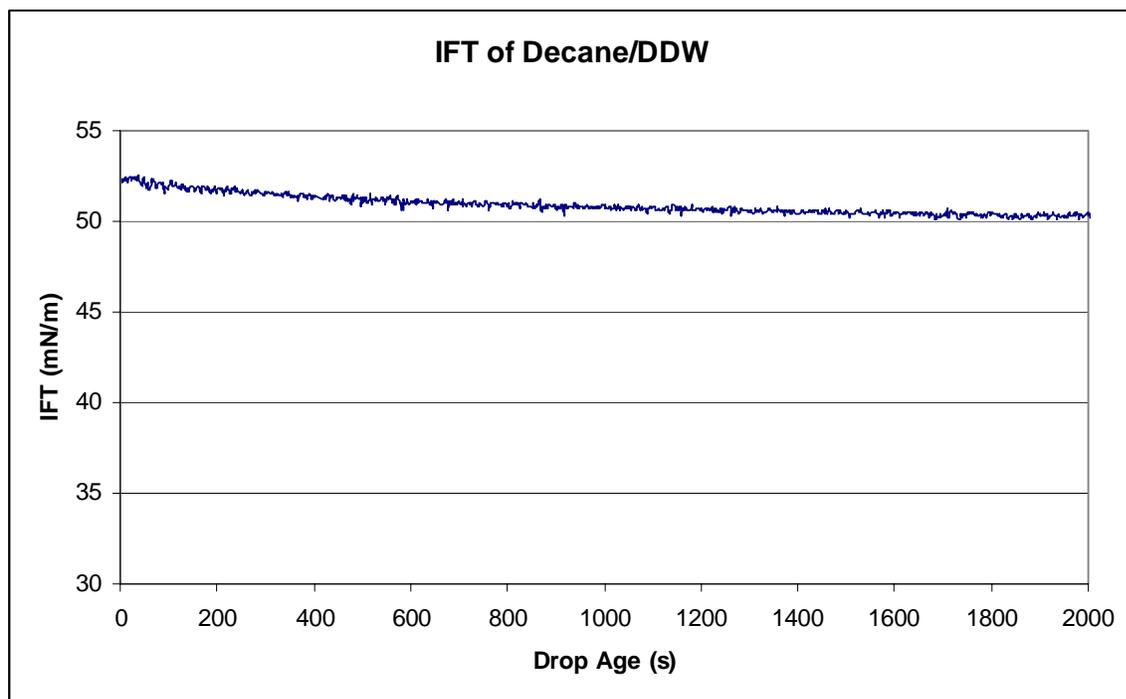


Figure 2. IFT of decane (as received) measured against DDW.

## Results and Discussion

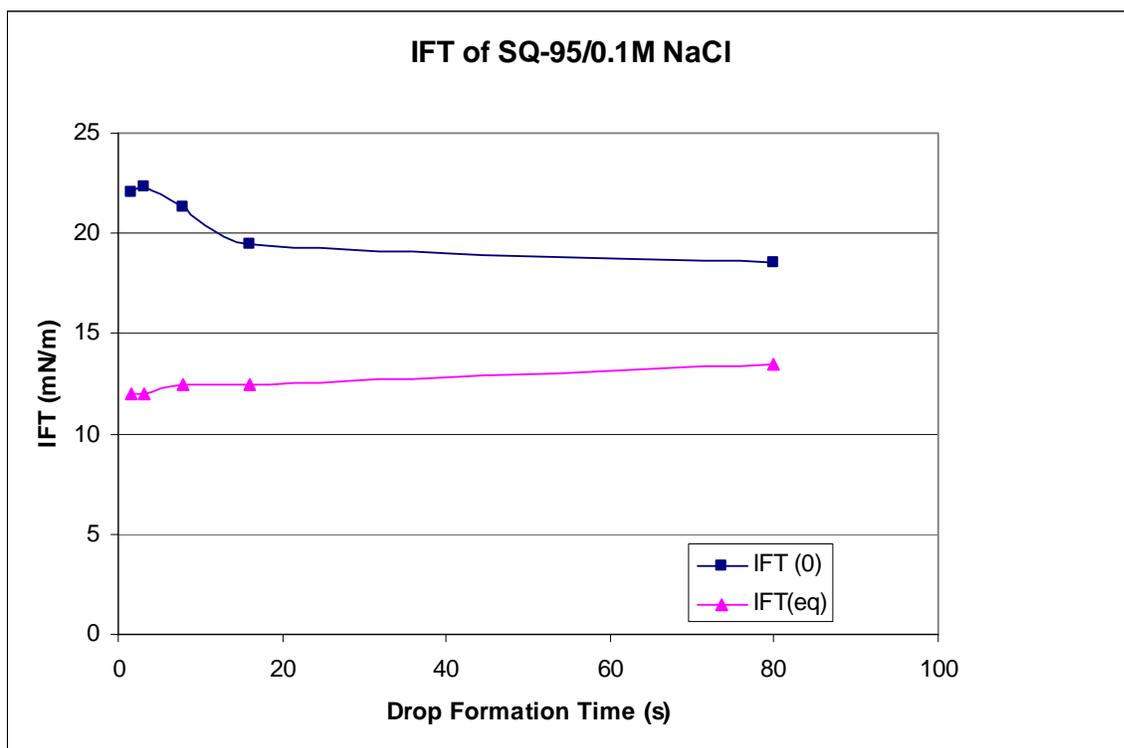
### *IFT of crude oil*

Crude oil IFT changes with interface age. Interfacially active molecules in crude oil are high molecular weight compounds that may rearrange slowly at the oil/water interface. In addition, there can be mass transfer of oil components that have some solubility in water or dissolution of water in the crude oil. Preequilibration of fluids reduces mass transfer, but may not eliminate it if the oil/water ratio is different than the ratio in the pendant drop configuration. Crude oil samples can include contaminants that add to the amount of extractable material and replace naturally interfacially active compounds at the oil/water interface. Depending on pH and composition of the aqueous phase, reactions such as saponification can occur that result in

extraction of additional oleic compounds into the aqueous phase. Monitoring IFT as a function of interface age can contribute information about the extent to which various dynamic processes are important for specific oil/brine combinations. First we examine some experimental details that can affect measured values of IFT, especially at short times. Once the experimental protocol has been developed, we use it to examine the impact of pH and composition of the aqueous phase on IFT for a range of crude oils.

### Drop formation time

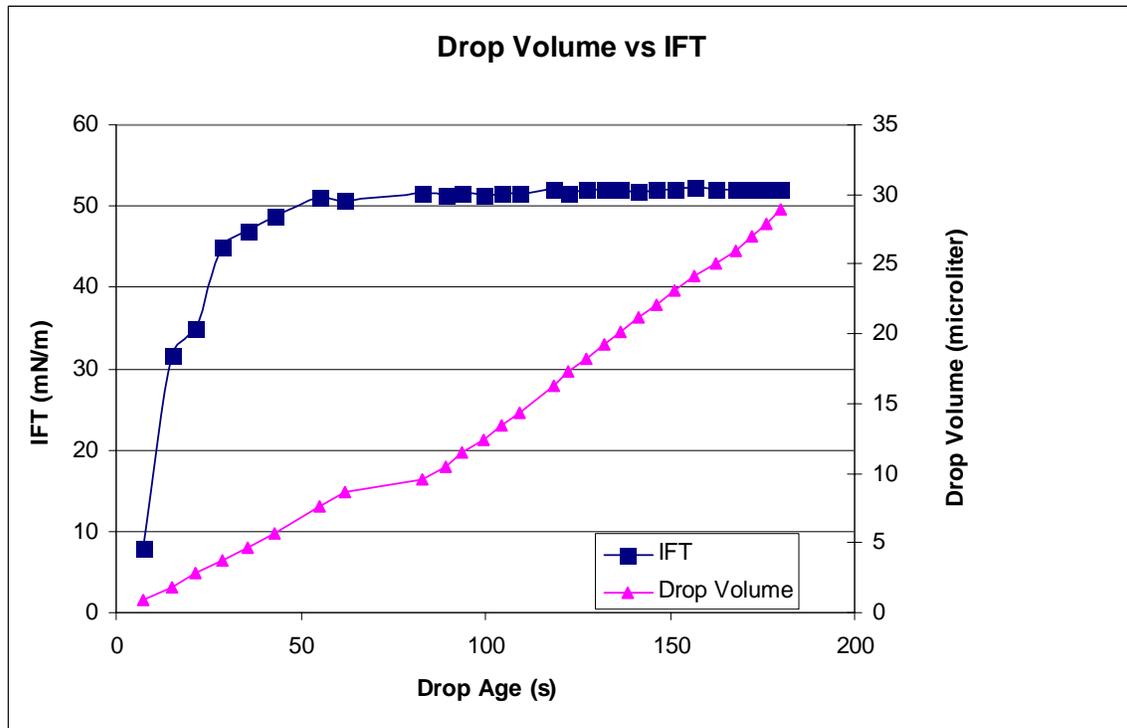
Capturing the initial and equilibrium IFT values of crude oils in water or brines is therefore of interest. It is not possible to measure an instantaneous initial value of IFT because there is a small amount of time required to form a drop. Figure 3 of the effect of varying drop formation time on the values of IFT(0) and IFT(eq) for SQ-95 oil in 0.1M NaCl. Drop volume was 10  $\mu\text{l}$ . Data recording began about 0.1 s after the preselected drop size was achieved. When the formation time was less than 3 s, IFT(0) was nearly constant at a value of 22.5 mN/m, then rapidly decreased when the formation time was increased. IFT(eq), taken in this study to be the IFT measured after 2000 s (about one-half hour) increased slightly with drop formation time, from about 12 to 13 mN/m. For the IFT measurements of crude oils in the remainder of this work, the drop formation time was always controlled at less than 2 s



**Figure 3** Impact of drop formation time on IFT.

### Impact of drop volume on IFT

In order to be used to measure IFT, a pendant drop must be large enough to allow both capillarity and gravity to influence drop shape. Fig. 4 shows IFT increasing as the volume of a drop of decane in 1 wt% NaCl was slowly increased. The drop was formed incrementally at a liquid delivery rate of  $0.1 \mu\text{l/s}$  to ensure that IFT measured was the same as or close to IFT(eq). It can be seen that when the drop volume was less than  $10 \mu\text{l}$ , the IFT increased rapidly with the continuous addition of decane to the drop. When the drop volume was larger than about  $12 \mu\text{l}$ , the IFT reached a constant value of about  $51 \text{ mN/m}$  and this value did not change with further addition of decane to the drop. The required minimum drop volume varies with IFT of the liquid pair and OD of the needle used to form the drop. Ten  $\mu\text{l}$  was sufficient volume for measurements of crude oil in water or brines using this needle.



**Figure 4** IFT of a drop of purified decane in 1% NaCl as a function of drop age for a drop whose volume is increasing at  $0.1 \mu\text{l/s}$ . The needle used to form the drop had an OD of 0.7 mm.

### Measurement protocol and modeling of IFT vs. time

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 seconds.

A model equation for IFT vs. time of asphaltene solutions was proposed by Jeribi et al. (2002), 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.

Equation 1 gives reasonable fits to data for a wide range of results. In many cases, however, the first IFT measurement, recorded within one or two seconds of drop formation was not well captured by fits to the rest of the interfacial tension vs. time data. In order to capture all of the observations, data records include the first measured IFT value as well as the initial and final (or equilibrium) values and  $\tau$  from the best fits. Data are summarized in the Appendix.

### Reproducibility

The dynamic tensions measurements of crude oil/brine IFT were generally quite reproducible, as shown by numerous examples in the Appendix, where duplicate measurements are marked by a superscript 2.

### Low tension limit

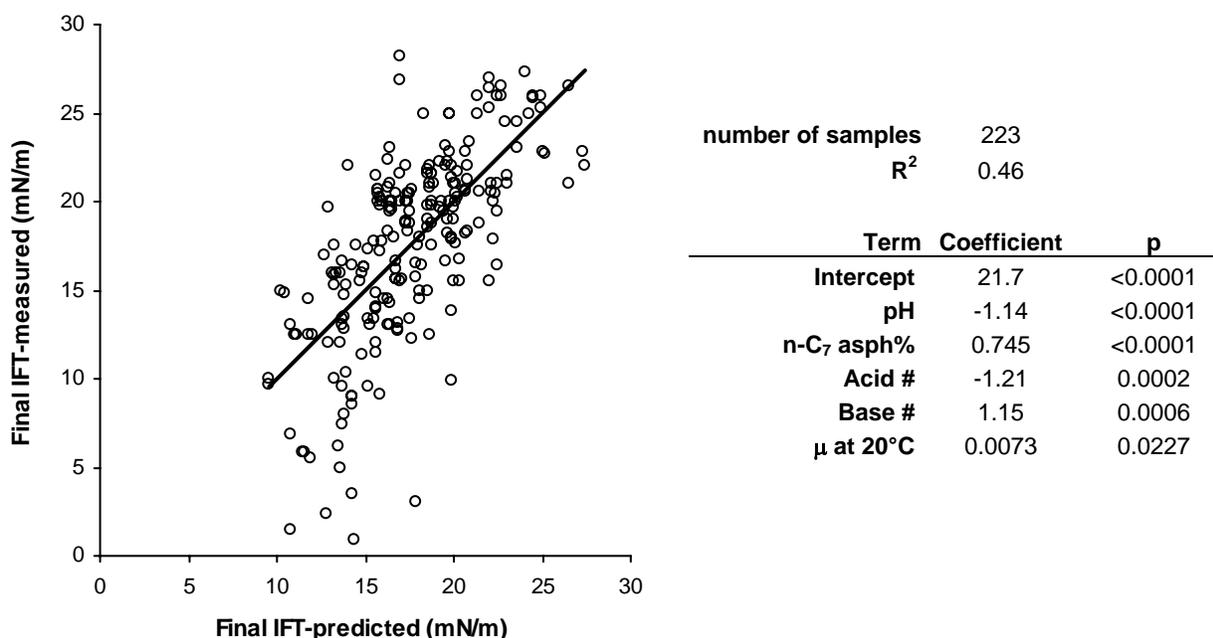
The pendant drop method of IFT measurement requires that a stable drop be formed. At tensions less than about 1 mN/m, oil streams continuously out of the drop-forming needle as shown in Fig. 5. Accurate measurements can be made by other methods, such as the spinning drop technique (Adamson and Gast, 1997), but such observations were beyond the scope of the present study.



**Figure 5. C-F2-00 streaming upwards when emerging from needle into pH = 10.9 0.1M NaCl.**

### An overview of IFT measurements for all crude oils and brines

Linear multivariate statistical analysis of all of the final or equilibrium IFT data in the Appendix produces the correlation shown in Fig. 6. Many crude oil properties accumulated in the CO-Wet database were examined. Density, refractive index, amounts of saturates, aromatics, and resins, and iso-electric point showed no significant correlation with IFT. The pH of the brine influences IFT, as expected from earlier work (Buckley, 1996) and reports in the literature (e.g., Reisberg and Doscher, 1956). 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.



**Figure 6. Equilibrium IFT values correlate with pH of the aqueous phase, the amount of n-C<sub>7</sub> asphaltenes, acid number, base number, and viscosity of each oil. The p values represent the probability that a given variable is not correlated with IFT; values of p less than 0.05 indicate significant correlation.**

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 dynamic 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. There is some coupling between the significance

of viscosity and acid number; if acid number was omitted from the parameter set, viscosity was not correlated significantly with IFT, although the reverse was not true. 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.

### ***Impact of pH on IFT of crude oil***

Two groups of seven crude oils each were selected for comparisons of the effect of pH on magnitude of IFT. Oils in the first group have low acid numbers (less than 0.1 mg KOH/g oil) and a typical range of base numbers. The second group contains oils with fairly high base and acid numbers.

#### Group 1: Low-acid-number oils

Seven crude oils with low acid numbers were designated as Group 1. As shown in Table 3, acid numbers ranged from 0.08 mg KOH/g oil to unmeasurable values (<0.01 mg KOH/g oil). Base numbers range from 0.11 to 2.5. IFT(0) and IFT(eq) are plotted in Fig. 7a-g for DDW and for 0.1 M NaCl with pH adjusted by addition of NaOH or HCl.

**Table 3. Properties of oils with low acid number and varying base number**

Oil ID	Acid #	Base #	n-C <sub>7</sub> asphaltene (wt%)	Viscosity (cP) at 20°C
C-R-01	<0.01	0.40	1.30	17.8
Minnelusa-02	0.01	2.01	8.75	58.2
B-1-00	0.04	0.85	0.62	4.7
Cottonwood-03	0.04	1.87	2.51	26.1
C-Lb-01	0.05	2.50	1.60	22.6
P-VE-00	0.05	1.54	3.43	16.9
C-Br-01	0.08	0.11	0.05	1.2

All oils in Group 1 have fairly constant IFT(0) and IFT(eq) when pH was lower than 6.4. At pH 8.9 for oils C-R-01 and C-Br-01 and at pH 10.8 for the remainder of the oils, the IFT(eq) decreased abruptly.

#### Group 2: Crude oils with high acid and base numbers

The seven crude oils in Group 2, listed in Table 4 in order of increasing acid number, have varying acid and base numbers. Plots of initial and equilibrium IFT as a function of pH in DDW and 0.1 M NaCl are given in Fig. 8a-g.

**Table 4. Properties of oils with high acid and base numbers**

Oil ID	Acid #	Base #	n-C <sub>7</sub> asphaltene (wt%)	Viscosity (cP) at 20°C
C-F2-03	0.70	1.32	1.97	28.6
E-1XD-00	1.56	2.98	2.54	137.4
LB-03	1.57	0.59	0.07	13.1
GOM(2)-00	2.02	1.79	8.63	122.3
C-K-01	2.44	5.19	3.46	393.6
E-1XO-00	3.42	2.57	0.76	15.3
Mars-P	3.92	2.30	4.77	481.1

For all oils, the lowest IFT values were obtained with the highest pH brines. Equilibrium IFT values are lower than initial IFTs. At the same pH, the IFT measured with 0.1 M NaCl were equal to or less than the IFT with DDW.

Group 1 oils, which had low acid numbers, had high-pH IFT values that were measurable by the pendant drop technique, whereas for six of the seven Group 2 oils, IFTs with the highest pH aqueous solutions, whether DDW or NaCl, were so low that a stable drop could not be formed.

Additional comparisons are shown in Fig. 9 where the equilibrium IFT values for each oil are replotted for Group 1 (Fig. 9a for DDW and 9b for 0.1 M NaCl) and Group 2 (Fig. 9c for DDW and 9d for 0.1 M NaCl) oils. It is difficult to see any clear trends either among the oils in either of these groups or between the two groups. There are oils whose IFT changes little with addition of NaCl in both groups (Minnelusa-02 in Fig. 7b, B-1-00 in Fig. 7c, LB-03 in Fig 8c, E-1XO-00 in Fig. 8f, and Mars-P in Fig. 8g). The maximum and minimum equilibrated values of IFT at near-neutral pH are similar for both groups, as are the differences between initial and equilibrated values of IFT. One difference was observed: the value of  $IFT(0) - IFT(eq)$  at acidic conditions was found to be a linear function of the log of viscosity, especially for Group 1 oils, as shown in Fig. 10.

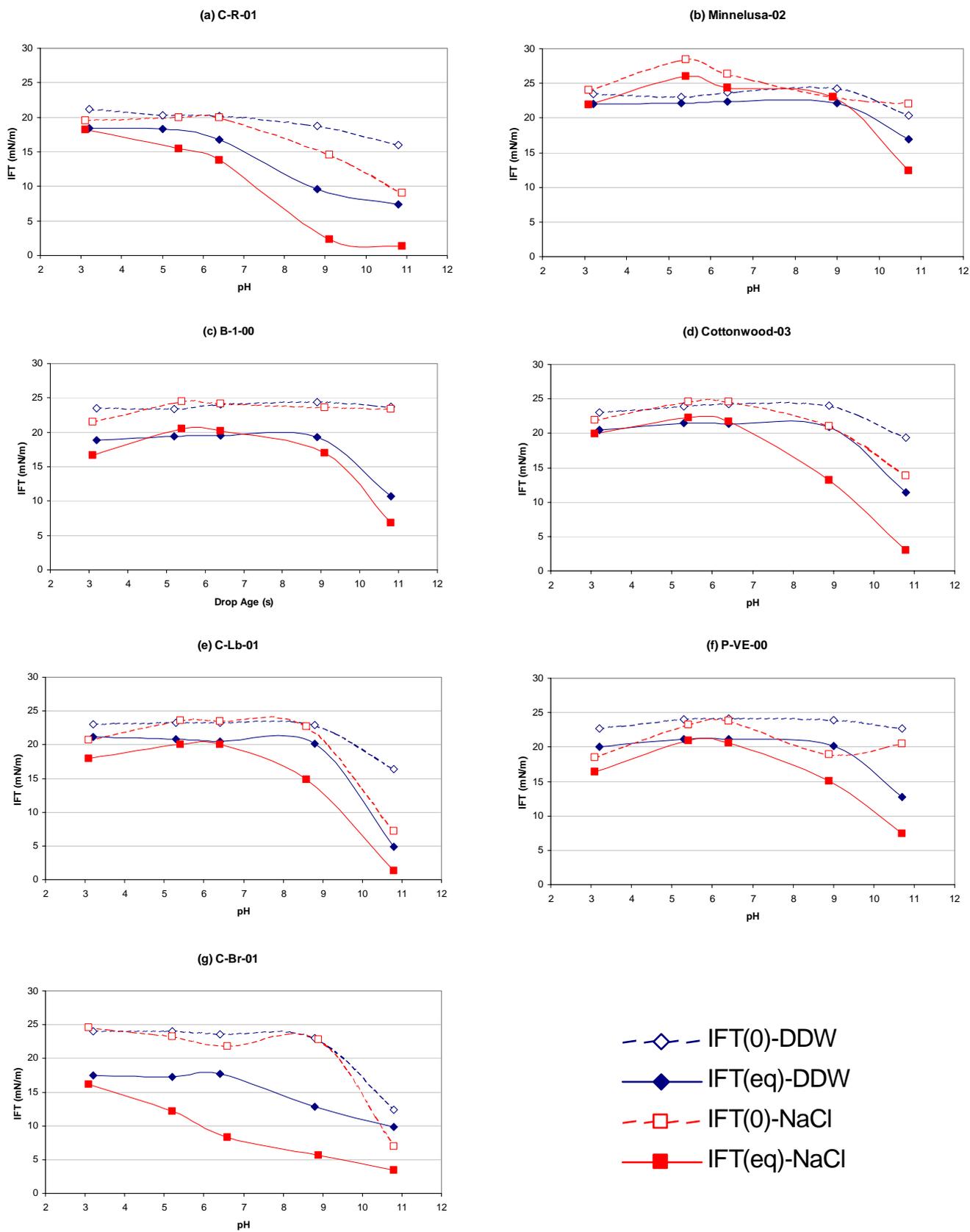


Figure 7. IFT as a function of pH for the low acid number crude oils in Group 1.

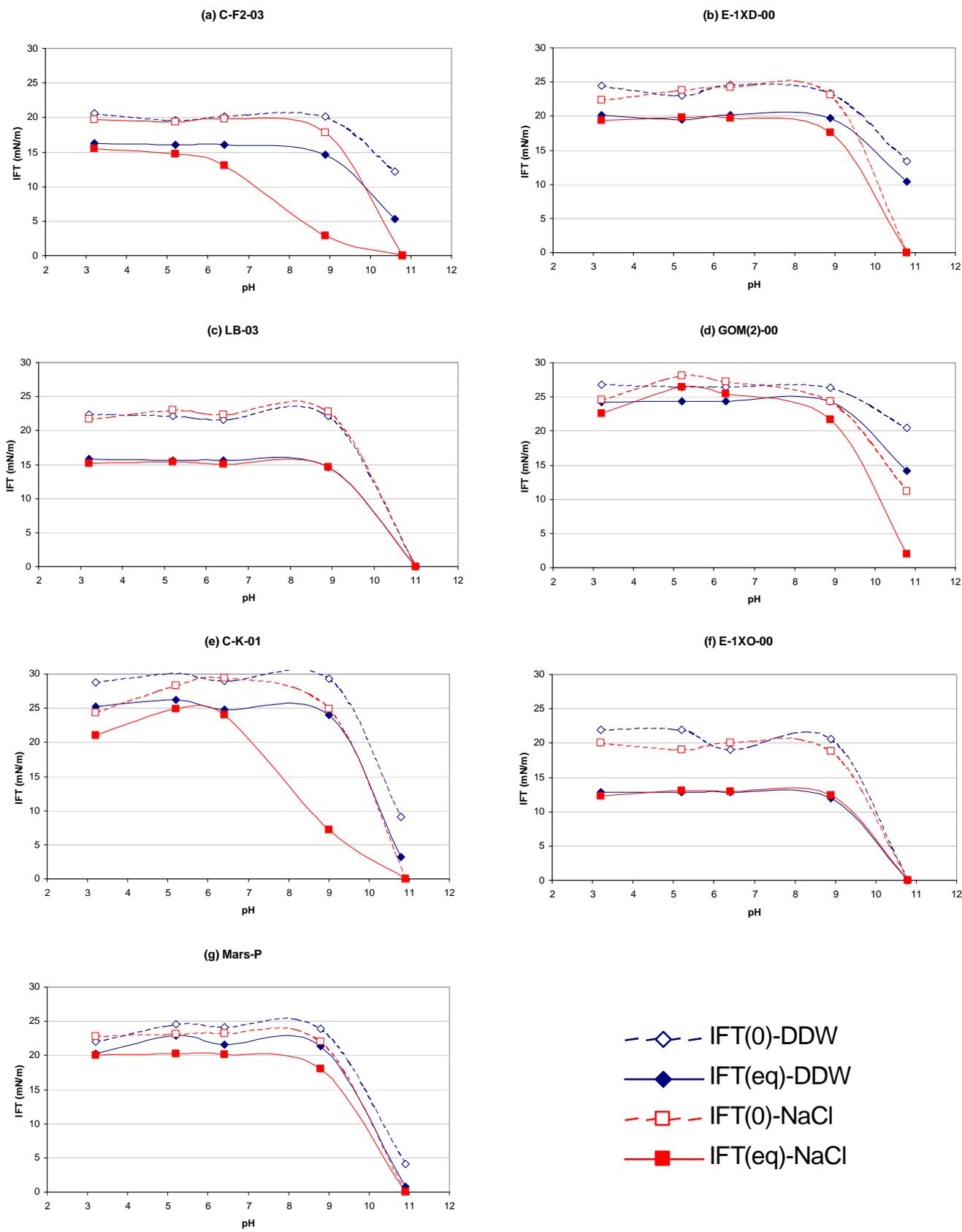


Figure 8. IFT as a function of pH for Group 2 crude oils, which have a range of acid and base numbers.

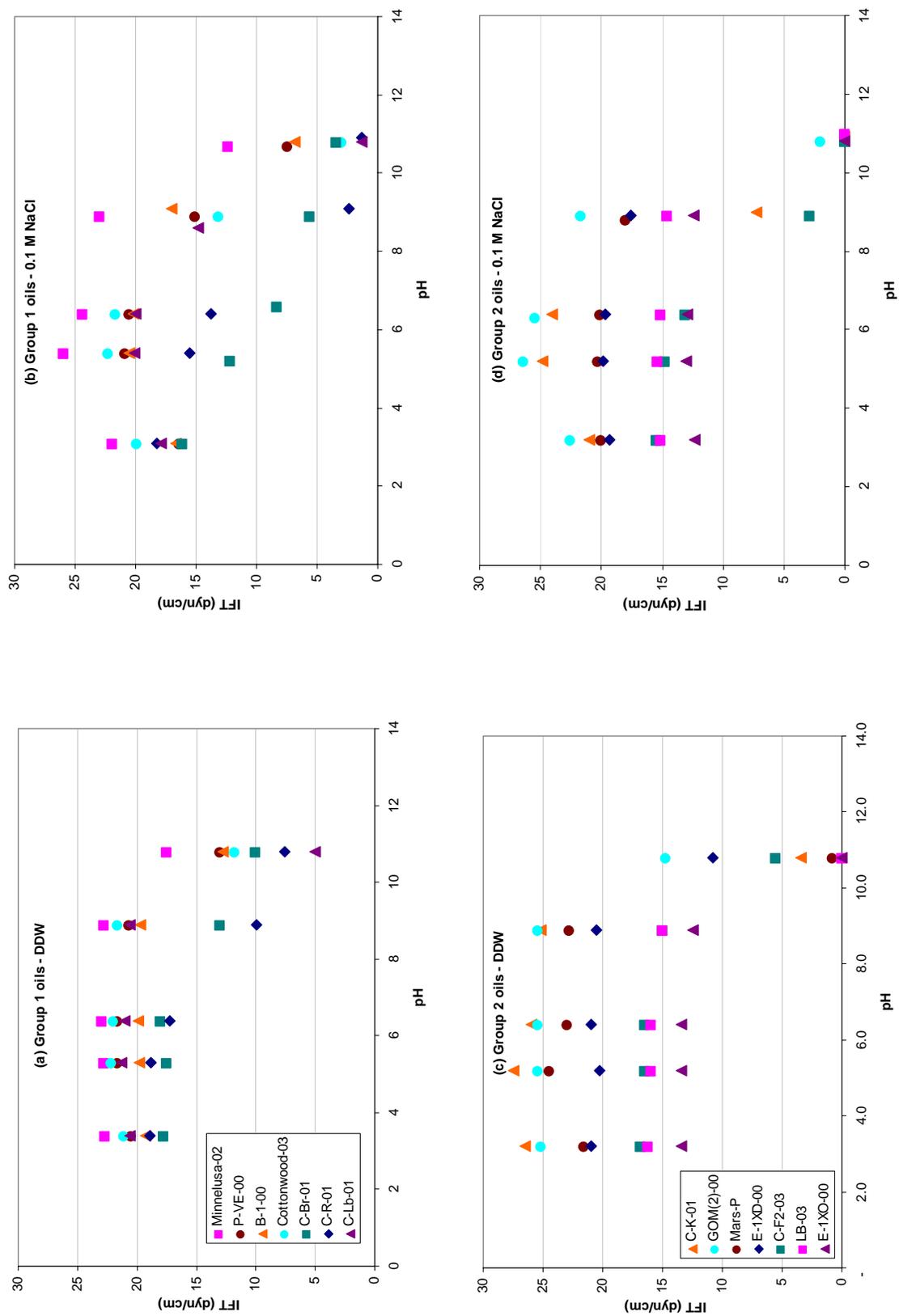
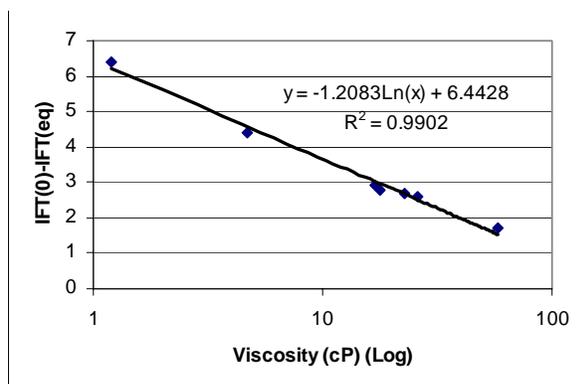
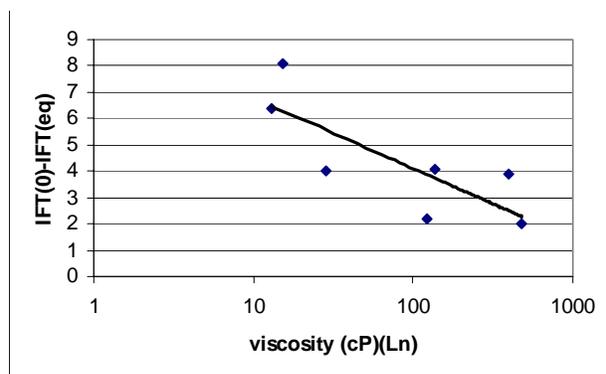


Figure 9. Summary of IFT(eq) data for Group 1 and 2 crude oils measured against pH-adjusted DDW and 0.1M NaCl solutions.



(a) Group 1, low acid number oils



(b) Group 2, higher acid and base number oils

Figure 10. At acidic conditions, the change in IFT with time correlates with log (viscosity).

### ***Comparison of IFT of different crude oils at constant pH***

Three pH ranges were selected for examination. Within each range, the data were further subdivided according to the composition of the aqueous phase, which falls into one of the following three categories:

- distilled water to which small amounts of HCl or NaOH were added to adjust pH,
- 0.1M NaCl to which small amounts of HCl or NaOH were added to adjust pH, and
- synthetic sea water (at near-neutral conditions only).

Crude oils tested at each of these conditions are indicated in Table 5. Table 6 summarizes fits to all of the data in each subgroup. For comparison, the same set of variables (n-C<sub>7</sub> asphaltenes, acid number, base number, and viscosity) was used for all of these correlations, although not all four of these variables are significant in every case. Values of p greater than 0.05 that indicate a higher probability of including that variable erroneously are indicated by the shaded boxes.

Removing those variables from the group would change the magnitudes of the remaining coefficients somewhat, but in no case were the signs of those coefficients changed.

**Table 5. Summary of crude oils tested in each pH and brine composition subgroup**

	DDW			0.1M NaCl			SSW
	3	6	9	3	6	9	6
B-1-00	x	x	x	x	x	x	
C-A1-00		x					x
C-AG-03		x					x
C-AL-03		x					x
C-Br-01	x	x	x	x	x	x	
C-F2-03	x	x	x	x	x	x	
C-GC-T1-03		x					x
C-K-01	x	x	x	x	x	x	
C-Lb-01	x	x	x	x	x	x	
C-R-01	x	x	x	x	x	x	
C-T-02		x					x
Cottonwood-03	x	x	x	x	x	x	
E-1XCO-01		x					x
E-1XD-00	x	x	x	x	x	x	x
E-1XFR-01		x					x
E-1XO-00	x	x	x	x	x	x	x
E-2XR-00		x					x
E-8XFR-01		x					x
E-BL-00		x					x
E-S1XCA-01		x					x
E-S1XG-01		x					x
E-S1XL-01		x					x
E-S3XR-01		x					x
GOM(2)-00	x	x	x	x	x	x	
Gulfaks-96		x					
LB-03	x	x	x	x	x	x	x
Mars-P	x	x	x	x	x	x	
Minnelusa-02	x	x	x	x	x	x	
Minnelusa-03		x					x
MY2-02	x	x	x	x	x	x	x
MY3-02	x	x	x	x	x	x	x
MY4-02	x	x	x	x	x	x	x
P-VE-00	x	x	x	x	x	x	
SQ-95	x	x	x				
S-Ven-39		x					x
S-Ven-40		x					x
S-Ven-41		x					x
Tensleep-99	x	x	x				
W-Br-03		x					x
W-Lo-03		x					

**Table 6. Summary of pH and brine composition subgroup correlations with standard variables**

	pH	n	R <sup>2</sup>	Intercept p value	n-C <sub>7</sub> asph% p value	Acid # p value	Base # p value	μ at 20°C p value
<b>DDW</b>	<b>3</b>	19	0.54	17.9338	0.4118	-1.7064	0.7572	0.0165
				<0.0001	0.0851	0.0136	0.2298	0.0242
	<b>6</b>	43	0.46	18.2559	0.4609	-1.6492	0.8548	0.0114
				<0.0001	0.0077	0.0009	0.0853	0.0103
	<b>9</b>	23	0.48	13.8502	0.7058	-1.3953	1.5510	0.0138
				<0.0001	0.0450	0.0784	0.0873	0.1206
<b>0.1M NaCl</b>	<b>3</b>	17	0.72	16.8837	0.6018	-1.2887	-0.0738	0.0145
				<0.0001	0.0017	0.0075	0.8584	0.0056
	<b>6</b>	20	0.69	11.5694	1.2503	-0.9129	2.0867	0.0017
				<0.0001	0.0005	0.2543	0.0148	0.8431
	<b>9</b>	15	0.48	6.3557	1.2070	0.6351	2.2863	-0.0037
				0.0227	0.0306	0.6269	0.1820	0.7986
<b>SSW</b>	<b>6</b>	25	0.28	14.7631	0.5721	-2.0157	1.3697	0.0092
				<0.0001	0.1405	0.0995	0.2555	0.3135

The best correlations with the standard group of oil properties were obtained for IFT measured with 0.1M NaCl solutions at all three pH conditions. For synthetic seawater, none of the standard variables were significant. The largest data sets were for measurements with distilled water results. Despite the availability of more data, correlations at all three pH conditions were not as good as those for the 0.1M NaCl solutions. Amount of n-C<sub>7</sub> asphaltene was below the p value threshold of 0.05 in five out of seven cases. In all cases, increasing acid number decreased IFT while increasing base number had the opposite effect. Higher IFT values were also associated with larger amounts of asphaltene and higher viscosities. Which variables were most significant depended on the pH and brine composition. Table 7 summarizes the coefficients calculated for the best fits with no variables included with p values greater than 0.09.

**Table 7. Best correlations for pH and brine composition subgroups**

pH	brine	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	DDW	0.52	18.7368	0.4463	-1.6022	0.0199
3	NaCl	0.74	16.8001	0.5983	-1.2971	0.0142
6	DDW	0.46	18.2559	0.4609	-1.6492	0.8548
6	NaCl	0.70	11.5666	1.2425		1.6910
9	DDW	0.42	13.1887	0.8981		1.4604
9	NaCl	0.56	6.3313	1.1645		2.5755

### Acidic conditions (pH ~ 3)

When the aqueous phase was acidic, amount of n-C<sub>7</sub> asphaltene, acid number, and viscosity were the most significant variables. Base number was not significant with or without added NaCl.

### Near-neutral conditions (pH ~ 6)

In NaCl solutions, base number and amount of n-C<sub>7</sub> asphaltene were the only oil properties that contributed significantly to IFT. In distilled water at near neutral pH, all the variables were significant at the  $p < 0.1$  level. Near-neutral DDW thus seems intermediate between lower and higher pH conditions in that all four variables have some influence. In synthetic seawater, the presence of divalent ions probably increases the importance of specific interactions with the crude oil that are not well correlated with any of the oil properties measured.

### Basic conditions (pH ~ 9)

In distilled water and NaCl solutions adjusted to pH 9, the amount of n-C<sub>7</sub> asphaltene and base numbers were the significant variables.

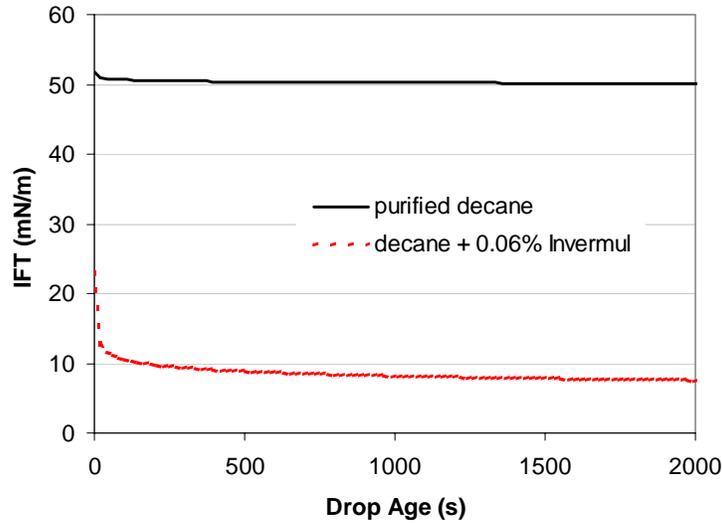
### Basic conditions (pH 10 and above)

Although numerical correlations cannot be made from this study because of the limitation on low IFT measurements by the pendant drop method, it is clear from comparison of Figs. 9b and 9d at high pH that acid numbers above those in Group 1 (i.e., above about 0.1 mg KOH/g oil) must be required to achieve very low tensions.

## ***Effect of crude oil contamination***

### Impact of a drilling mud additive on the IFT of decane

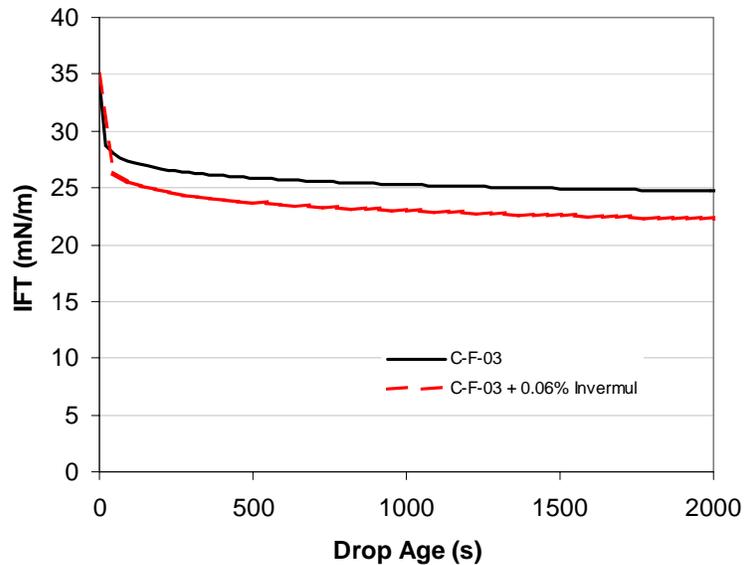
Invermul is a blend of oxidized tall oil and polyaminated fatty acid surfactants that is commonly added to oil-based drilling fluids to promote emulsification of water. Fig. 11 shows a comparison of IFT measured against DDW of decane with and without the addition of 0.06 wt% Invermul. Addition of a small amount of Invermul to decane dramatically decreased the both initial and final IFT.



**Fig. 11. Impact of drilling mud additive on the IFT of decane.**

Impact of Drilling Mud Additive on the IFT of C-F-03 Crude Oil

The impact of drilling mud additive on IFT of a crude oil was similarly tested by adding 0.06% wt Invermul to C-F-03. The IFT of C-F-03 in DDW with and without Invermul is shown in Fig.12. The IFT(0) were all about the same at 35mN/m for the three measurements. The IFT(eq) for the sample with Invermul was about 3 mN/m lower than that of the crude oil alone. The emulsifier had an impact on IFT but not as much as observed with decane. There appears to be a “deactivation” effect of the polar constituents in the oil that probably varies from one oil to another.



**Fig. 12 Impact of drilling mud additive on the IFT of C-F-03 oil.**

### Effect of an unknown surface-active contaminant

IFT measurements vs. pH are shown for four additional oil samples, all from the same reservoir: MY1-02, MY2-02, MY3-02, and MY4-02 (Fig. 13). IFTs were reported for these oil samples by Hirasaki and Zhang (2003) measured in carbonate formation brine with a high concentration of bicarbonate (35mmole/L). The IFT values reported after 30 min for these four oil samples were about 8, 14, 27, and 27 mN/m, respectively. Based on these results, MY1-02 and MY2-02 were judged to be contaminated because of the low IFT values. Fig. 13 shows the effect of varying pH on each of these oil samples measured with pH adjusted distilled water and 0.1M NaCl. The decrease in equilibrium IFT of MY1-02 with increasing pH in 0.1M NaCl, even at near-neutral conditions, is quite different from the behavior of the other three samples. MY1-02 was an outlier in nearly all correlations, as shown in Fig. 14 for measurements with near-neutral, 0.1M NaCl solutions. MY2-02 is much closer to the correlation lines, suggesting that its IFT may have been lower than others in the Hirasaki and Zhang study because of the sensitivity of IFT to high pH, whereas our data tend to support the conclusion that MY1-02 contains surface-active contaminants. MY1-02 has therefore been excluded from all the correlations reported here (except that in Fig. 14). If MY1-02 was removed from the data set, the value of  $R^2$  increased to 0.7.

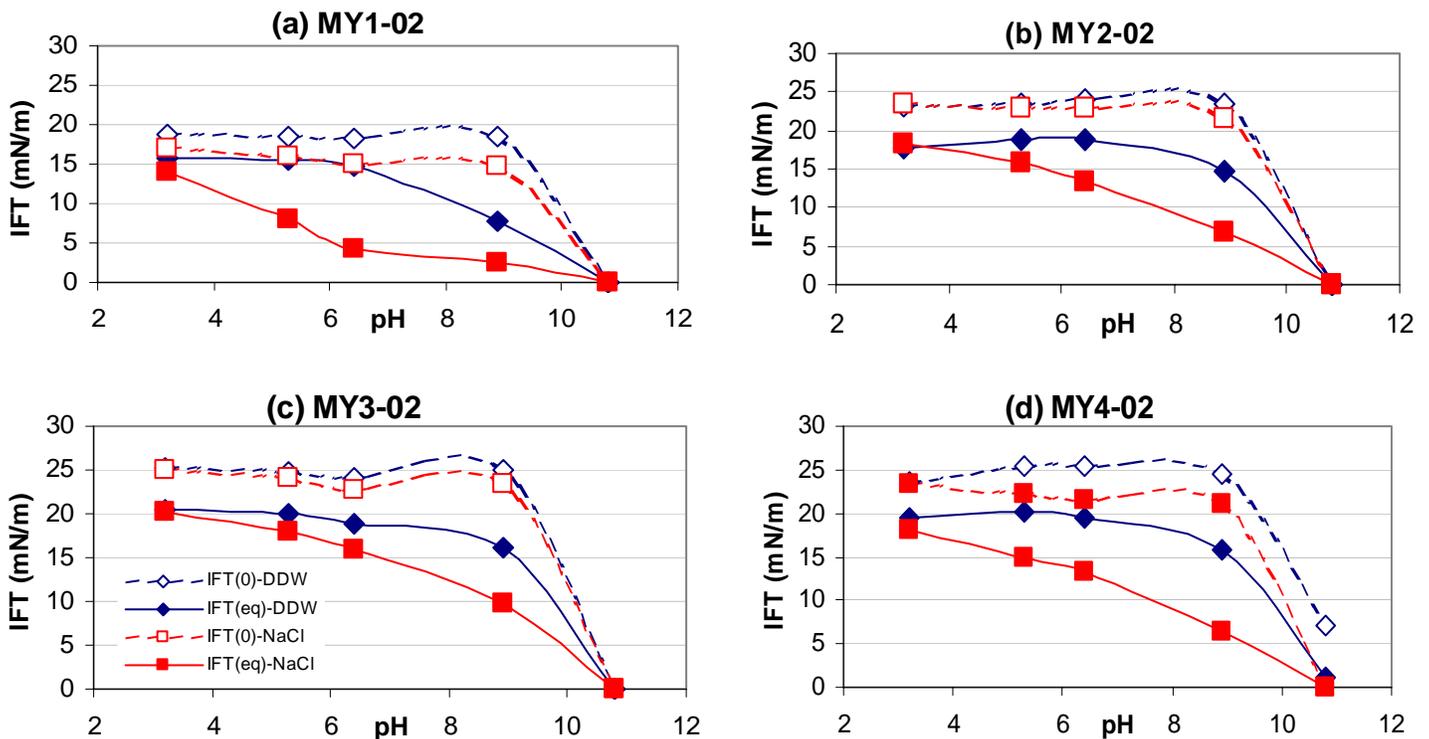


Figure 13. IFT of MY oils supplied by Rice University as a function of brine composition and pH.

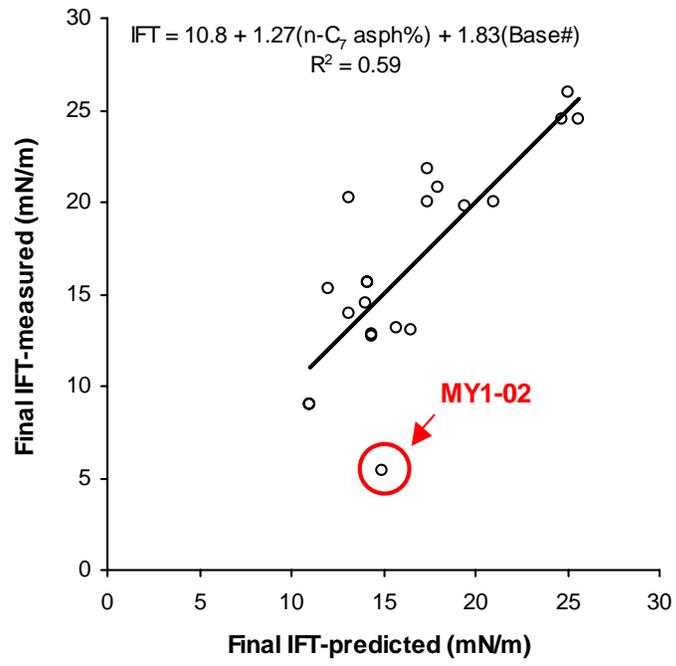


Figure 14. pH6, 0.1M NaCl correlation showing that MY1-02 is an outlier.

## 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.
- 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.
- Addition of surface-active contaminants reduces the IFT of both decane and crude oil, but the effect is much more dramatic for decane.
- Judging by IFT vs pH trends and by multivariate statistical correlations, oil MY1-02 probably is contaminated with materials that affect its IFT.

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## Appendix. IFT Measurements and Fits to Experimental Data

oil sample	aqueous phase composition	pH	IFT (mN/m)			$\tau$ (s)	$r^2$
			initial measured	initial fit	final		
B-1-00	0.1M NaCl	3.1	21.5	18.5	16.6	160	0.80
B-1-00	0.1M NaCl	5.6	24.1	22.0	20.5	260	0.87
B-1-00	0.1M NaCl	6.4	24.2	22.5	20.3	160	0.85
B-1-00	0.1M NaCl	9.1	23.6	22.0	17.0	100	0.91
B-1-00	0.1M NaCl	10.8	19.1	13.0	6.9	30	0.84
B-1-00	distilled water	3.2	24.0	22.5	19.4	200	0.89
B-1-00	distilled water	5.0	23.9	22.5	20.0	250	0.88
B-1-00	distilled water	6.3	24.5	23.0	20.0	200	0.88
B-1-00	distilled water	8.9	24.8	22.5	19.7	200	0.91
B-1-00	distilled water	10.8	21.5	19.0	13.0	150	0.91
C-A1-00	distilled water	6.4	24.8	24.0	22.3	180	0.78
C-A1-00	SSW <sup>1</sup>	6.4	23.6	22.2	19.7	330	0.93
C-AG-03	distilled water	6.4	23.2	22.0	16.3	90	0.97
C-AG-03	SSW	6.4	20.6	20.2	16.3	75	0.92
C-AL-03	distilled water	6.4	28.2	28.5	26.0	400	0.69
C-AL-03	SSW	6.4	27.9	28.0	25.8	400	0.67
C-Br-01	0.1M NaCl	3.1	22.0	19.0	16.4	100	0.68
C-Br-01	0.1M NaCl	5.4	20.3	18.0	12.0	180	0.92
C-Br-01 <sup>2</sup>	0.1M NaCl	6.6	18.8	16.0	9.0	300	0.97
C-Br-01 <sup>2</sup>	0.1M NaCl	6.6	20.6	16.0	9.0	300	0.93
C-Br-01	0.1M NaCl	9.0	21.4	19.0	5.8	220	0.89
C-Br-01	0.1M NaCl	10.8	3.4				
C-Br-01	distilled water	3.2	22.3	21.0	18.0	60	0.85
C-Br-01	distilled water	5.4	22.7	21.0	17.8	100	0.88
C-Br-01	distilled water	6.4	22.8	21.0	17.5	190	0.85
C-Br-01 <sup>2</sup>	distilled water	8.7	23.3	20.0	14.5	350	0.94
C-Br-01 <sup>2</sup>	distilled water	8.7	22.0	20.0	12.5	600	0.93
C-Br-01 <sup>2</sup>	distilled water	10.7	10.0		9.7		
C-Br-01 <sup>2</sup>	distilled water	10.7	10.0		10.0		
C-F2-03	0.1M NaCl	3.2	19.2	18.0	15.5	150	0.85
C-F2-03	0.1M NaCl	5.2	19.4	18.0	14.9	130	0.88
C-F2-03	0.1M NaCl	6.3	19.8	17.0	13.2	340	0.95
C-F2-03	0.1M NaCl	9.1	17.6				
C-F2-03	0.1M NaCl	10.9	nm <sup>3</sup>				
C-F2-03	distilled water	3.2	20.7	19.0	16.7	200	0.87
C-F2-03	distilled water	5.43	19.6	19.0	16.5	160	0.88
C-F2-03	distilled water	6.35	20.6	19.5	16.6	180	0.90
C-F2-03	distilled water	8.85	20.7	19.5	15.3	190	0.89
C-F2-03	distilled water	10.6	8		5.5		
C-GC-T1-03	distilled water	6.4	28.2	27.0	25.0	300	0.88
C-GC-T1-03	SSW	6.4	25.4	25.4	22.8	210	0.86
C-K-01	0.1M NaCl	3.2	24.4	23.0	21.0	340	0.65

oil sample	aqueous		IFT (mN/m)			$\tau$ (s)	$r^2$
	phase composition	pH	initial	initial	final		
			measured	fit			
C-K-01	0.1M NaCl	5.2	27.7	27.0	25.0	250	0.15
C-K-01	0.1M NaCl	6.3	29.5	28.0	24.5	320	0.51
C-K-01	0.1M NaCl	9.1	21.3				
C-K-01	0.1M NaCl	10.9	nm				
C-K-01	distilled water	3.2	29.5	29.0	26.5	250	0.56
C-K-01	distilled water	5.3	30.6	30.0	27.3	400	0.62
C-K-01	distilled water	6.5	29.8	29.0	26.0	400	0.69
C-K-01	distilled water	9.1	30.5	29.0	25.0	600	0.84
C-K-01	distilled water	10.8	7.7	7.0	3.0	60	0.93
C-Lb-01	0.1M NaCl	3.1	20.7	19.0	17.9	100	0.78
C-Lb-01	0.1M NaCl	5.4	23.6	21.5	20.0	200	0.58
C-Lb-01	0.1M NaCl	6.2	23.5	22.0	20.0	350	0.86
C-Lb-01	0.1M NaCl	8.6	22.7	22.0	14.5	350	0.90
C-Lb-01	0.1M NaCl	10.8	4.3				
C-Lb-01	distilled water	3.2	23.6	22.0	20.6	200	0.78
C-Lb-01	distilled water	5.2	23.9	23.0	21.3	180	0.76
C-Lb-01	distilled water	6.3	23.9	23.0	21.0	120	0.80
C-Lb-01	distilled water	8.9	23.5	22.0	20.5	200	0.79
C-Lb-01	distilled water	10.8	16.8	15.0	5.0	200	0.90
C-R-01	0.1M NaCl	3.1	19.6	19.0	18.2	80	0.59
C-R-01	0.1M NaCl	5.4	19.3	18.0	15.6	80	0.82
C-R-01	0.1M NaCl	6.6	17.7	17.5	13.9	220	0.93
C-R-01	0.1M NaCl	9.1	13.0	10.0	2.4	60	0.96
C-R-01	0.1M NaCl	10.9	8.2	9.0	1.5	9	0.99
C-R-01	distilled water	3.1	20.2	20.0	19.0	40	0.61
C-R-01	distilled water	5.0	20.2	20.0	18.8	40	0.63
C-R-01	distilled water	5.2	20.0	20.0	18.9	40	0.48
C-R-01	distilled water	6.5	19.6	19.0	17.2	150	0.84
C-R-01	distilled water	8.8	19.2	17.0	10.0	100	0.98
C-R-01	distilled water	10.8	12.1				
C-T-02	distilled water	6.4	32.1	31.0	28.2	270	0.85
C-T-02	SSW	6.4	29.4	29.5	26.9	250	0.87
Cottonwood-03	0.1M NaCl	3.1	21.5	21.5	20.0	100	0.89
Cottonwood-03	0.1M NaCl	5.5	23.6	23.5	22.2	100	0.54
Cottonwood-03	0.1M NaCl	6.4	24.6	24.0	21.8	100	0.68
Cottonwood-03 <sup>2</sup>	0.1M NaCl	9.0	21.0	20.0	14.0	100	0.77
Cottonwood-03 <sup>2</sup>	0.1M NaCl	9.0	21.0	20.0	14.8	60	0.89
Cottonwood-03	0.1M NaCl	10.8	11.9				
Cottonwood-03	distilled water	3.2	23.7	23.0	21.0	220	0.75
Cottonwood-03	distilled water	5.2	24.6	24.0	22.0	240	0.74
Cottonwood-03	distilled water	6.3	25.0	24.0	22.0	200	0.49
Cottonwood-03	distilled water	8.9	24.8	23.5	21.5	400	0.75
Cottonwood-03	distilled water	10.8	20.0	18.0	12.0	150	0.93
Cottonwood-03	RB-Minnelusa	6.4	24.4	23.5	18.5	300	0.95
E-1XCO-01	distilled water	6.4	25.6	25.5	21.6	45	0.87

oil sample	aqueous		IFT (mN/m)			$\tau$ (s)	$r^2$
	phase composition	pH	initial	initial	final		
			measured	fit			
E-1XCO-01	SSW	6.4	22.8	22.7	20.0	140	0.90
E-1XD-00	0.1M NaCl	3.2	22.3	21.5	19.4	60	0.52
E-1XD-00	0.1M NaCl	5.2	23.8	23.0	20.2	100	0.58
E-1XD-00	0.1M NaCl	6.4	24.2	22.5	19.8	180	0.62
E-1XD-00	0.1M NaCl	8.9	23.1	21.5	17.8	200	0.69
E-1XD-00	0.1M NaCl	10.8	nm				
E-1XD-00	distilled water	3.2	25.4	24.5	21.0	150	0.81
E-1XD-00	distilled water	5.3	24.0	22.5	20.5	190	0.75
E-1XD-00 <sup>2</sup>	distilled water	6.4	24.3	24.5	21.0	120	0.77
E-1XD-00 <sup>2</sup>	distilled water	6.4	24.6	25.0	21.6	130	0.73
E-1XD-00	distilled water	9.1	24.3	23.5	20.7	150	0.75
E-1XD-00	distilled water	10.7	13.5		10.3		
E-1XD-00	SSW	6.4	23.2	22.0	18.8	250	0.89
E-1XFR-01	distilled water	6.4	20.5	20.0	17.3	130	0.78
E-1XFR-01	SSW	6.4	18.3	18.1	9.5	200	0.98
E-1XO-00	0.1M NaCl	3.1	18.5	16.0	12.2	100	0.81
E-1XO-00	0.1M NaCl	5.2	19.1	17.0	13.0	250	0.89
E-1XO-00	0.1M NaCl	6.6	20.1	17.0	13.0	250	0.89
E-1XO-00	0.1M NaCl	8.9	18.1	17.0	12.5	200	0.93
E-1XO-00	0.1M NaCl	10.9	nm				
E-1XO-00	distilled water	3.1	20.0	18.0	13.4	220	0.89
E-1XO-00	distilled water	5.0	19.9	17.0	13.4	250	0.89
E-1XO-00	distilled water	5.2	19.5	17.0	13.4	150	0.85
E-1XO-00	distilled water	6.4	18.6	18.5	14.7	300	0.92
E-1XO-00	distilled water	6.5	19.8	17.0	13.4	250	0.91
E-1XO-00	distilled water	8.0	17.6	16.0	12.5	200	0.87
E-1XO-00	distilled water	8.8	18.8	16.5	12.5	250	0.90
E-1XO-00	distilled water	10.8	nm				
E-1XO-00	SSW	6.4	13.5	16.9	12.8	200	0.89
E-2XR-00	distilled water	6.4	21.8	23.5	20.4	80	0.61
E-2XR-00	SSW	6.4	22.0	21.8	18.3	190	0.91
E-8XFR-01	distilled water	6.4	19.4	18.5	16.4	120	0.82
E-8XFR-01	SSW	6.4	17.4	16.2	8.6	300	0.97
E-BL-00	distilled water	6.4	21.4	21.3	19.8	80	0.47
E-BL-00	SSW	6.4	21.2	20.7	19.0	130	0.73
E-S1XCA-01	distilled water	6.4	20.1	20.5	18.0	200	0.74
E-S1XCA-01	SSW	6.4	17.8	17.5	13.8	100	0.73
E-S1XG-01	distilled water	6.4	27.1	28.0	20.0	270	0.97
E-S1XG-01	SSW	6.4	24.7	24.9	19.6	245	0.95
E-S1XL-01	distilled water	6.4	24.0	23.0	20.8	120	0.69
E-S1XL-01	SSW	6.4	21.2	20.7	18.3	250	0.93
E-S3XR-01	distilled water	6.4	24.0	23.0	20.0	225	0.81
E-S3XR-01	SSW	6.4	22.1	21.6	18.8	120	0.83
GOM(2)-00	0.1M NaCl	3.2	24.6	23.5	22.8	250	0.18
GOM(2)-00	0.1M NaCl	5.2	27.6	27.5	26.5	200	0.03

oil sample	aqueous		IFT (mN/m)			$\tau$ (s)	$r^2$
	phase composition	pH	initial	initial	final		
			measured	fit			
GOM(2)-00	0.1M NaCl	6.3	27.3	26.5	25.9	150	0.00
GOM(2)-00	0.1M NaCl	8.8	24.3	24.0	21.6	150	0.26
GOM(2)-00	0.1M NaCl	10.9	11.2				
GOM(2)-00	distilled water	3.2	27.0	26.5	25.3	100	0.33
GOM(2)-00	distilled water	5.4	27.5	26.5	26.0	250	0.13
GOM(2)-00	distilled water	6.4	27.5	26.5	25.0	1000	0.43
GOM(2)-00	distilled water	9.1	27.1	26.0	25.0	250	0.02
GOM(2)-00	distilled water	10.7	15.0		20.0		
Gulfaks-96	distilled water	6.4	23.4	22.0	19.8	200	0.82
Gulfaks-96	RB-Minnelusa	6.4	21.2	19.4	9.1	230	0.95
Gulfaks-96	SSW-HCO <sub>3</sub> <sup>4</sup>	7.8	20.0	18.2	3.5	60	0.96
LB-03	0.1M NaCl	3.2	21.4	19.5	15.5	150	0.90
LB-03	0.1M NaCl	5.2	21.4	19.5	15.5	150	0.93
LB-03	0.1M NaCl	6.4	21.7	19.5	15.3	150	0.93
LB-03	0.1M NaCl	8.9	21.6	19.5	14.8	150	0.94
LB-03	0.1M NaCl	11.0	nm				
LB-03	distilled water	3.4	22.2	19.5	16.2	330	0.94
LB-03	distilled water	5.1	22.0	19.5	16.0	330	0.94
LB-03	distilled water	6.5	21.8	19.5	16.0	300	0.95
LB-03	distilled water	9.1	22.7	19.0	15.0	250	0.95
LB-03	distilled water	10.8					0.00
LB-03	SSW	6.4	21.4	20.7	15.8	150	0.97
Mars-P	0.1M NaCl	3.2	22.1	23.0	21.0	50	0.01
Mars-P	0.1M NaCl	5.2	23.2	23.0	20.7	100	0.27
Mars-P	0.1M NaCl	6.4	19.4	22.0	20.0	250	0.19
Mars-P	0.1M NaCl	8.8	17.5	21.5	18.0	200	0.51
Mars-P	0.1M NaCl	10.9	nm				
Mars-P	distilled water	3.2	22.8	22.5	21.5	300	0.24
Mars-P	distilled water	5.1	26.1	25.0	23.4	300	0.47
Mars-P	distilled water	6.2	25.6	25.0	23.2	150	0.42
Mars-P	distilled water	9.1	24.8	24.5	22.4	300	0.38
Mars-P	distilled water	10.8	4.3	4.5	0.9	25	0.99
Minnelusa-02	0.1M NaCl	3.1	24.0	23.8	22.0	100	0.55
Minnelusa-02	0.1M NaCl	5.2	28.5	28.0	26.0	100	0.16
Minnelusa-02	0.1M NaCl	6.4	25.9	26.0	24.5	100	0.18
Minnelusa-02	0.1M NaCl	8.9	22.5	23.0	22.0	100	0.11
Minnelusa-02	0.1M NaCl	10.7	20.7	20.0	12.5	20	0.83
Minnelusa-02	distilled water	3.2	24.9	24.0	22.8	100	0.37
Minnelusa-02	distilled water	5.0	24.2	23.5	22.7	100	0.36
Minnelusa-02	distilled water	6.4	22.2	24.0	23.0	100	0.09
Minnelusa-02	distilled water	9.0	25.0	24.5	22.8	100	0.54
Minnelusa-02	distilled water	10.7	20.0		17.5		
Minnelusa-03	distilled water	6.4	29.9	29.0	27.0	500	0.87
Minnelusa-03	RB-Minnelusa	6.4	28.5	28.0	26.4	300	0.56
Minnelusa-03	SSW	6.4	27.2	26.7	25.3	500	0.52

oil sample	aqueous		IFT (mN/m)			$\tau$ (s)	$r^2$
	phase composition	pH	initial	initial	final		
			measured	fit			
MY1-02	0.1M NaCl	3.2	16.3	15.1	13.6	110	0.85
MY1-02	0.1M NaCl	5.0	15.0	13.6	8.3	100	0.77
MY1-02	0.1M NaCl	6.0	13.7	11.7	5.4	400	0.97
MY1-02	0.1M NaCl	9.0	13.3	11.7	2.5	100	0.99
MY1-02	0.1M NaCl	10.7	nm				
MY1-02	distilled water	3.2	19.3	18.0	16.2	150	0.87
MY1-02	distilled water	5.4	18.2	17.5	16.0	100	0.73
MY1-02	distilled water	6.4	18.7	17.0	15.1	320	0.90
MY1-02	distilled water	8.8	18.0	16.0	8.0	400	0.96
MY1-02	distilled water	10.8	nm				
MY1-02	SSW	6.4	8.8	7.5	2.4	220	0.97
MY2-02	0.1M NaCl	3.2	21.9	20.9	17.9	350	0.90
MY2-02	0.1M NaCl	5.0	20.9	19.5	15.8	300	0.91
MY2-02	0.1M NaCl	6.4	21.0	20.0	14.5	300	0.91
MY2-02	0.1M NaCl	8.7	19.9	18.5	7.4	500	0.98
MY2-02	0.1M NaCl	10.7	nm				
MY2-02	distilled water	3.2	23.7	22.0	19.0	250	0.85
MY2-02	distilled water	5.4	24.1	23.0	19.4	300	0.88
MY2-02	distilled water	6.4	24.0	22.0	19.4	250	0.86
MY2-02	distilled water	8.8	23.3	22.0	16.0	500	0.96
MY2-02	distilled water	10.8	nm				
MY2-02	SSW	6.4	21.5	20.5	13.0	300	0.94
MY3-02	0.1M NaCl	3.2	23.8	22.4	19.7	190	0.80
MY3-02	0.1M NaCl	5.0	23.4	20.9	17.5	250	0.88
MY3-02 <sup>2</sup>	0.1M NaCl	6.1	22.1	20.4	15.6	300	0.91
MY3-02 <sup>2</sup>	0.1M NaCl	6.1	22.8	20.0	15.6	400	0.79
MY3-02	0.1M NaCl	8.8	22.7	19.0	9.5	550	0.97
MY3-02	0.1M NaCl	10.7	nm				
MY3-02	distilled water	3.2	25.2	23.5	21.0	300	0.89
MY3-02	distilled water	5.4	24.4	23.5	20.5	200	0.78
MY3-02	distilled water	6.4	24.4	24.5	21.0	130	0.78
MY3-02	distilled water	8.7	24.7	23.0	16.6	500	0.98
MY3-02	distilled water	10.7	nm				
MY3-02	SSW	6.4	21.9	20.5	14.3	350	0.96
MY4-02	0.1M NaCl	3.2	22.6	20.4	17.6	300	0.88
MY4-02	0.1M NaCl	5.0	20.6	19.0	14.5	250	0.92
MY4-02 <sup>2</sup>	0.1M NaCl	6.0	20.4	18.5	12.7	450	0.94
MY4-02 <sup>2</sup>	0.1M NaCl	6.0	19.8	18.5	12.8	500	0.95
MY4-02	0.1M NaCl	9.0	20.4	17.5	6.2	350	0.99
MY4-02	0.1M NaCl	10.8	nm				
MY4-02	distilled water	3.2	24.4	23.0	20.0	300	0.89
MY4-02	distilled water	5.4	26.7	24.0	20.7	300	0.89
MY4-02 <sup>2</sup>	distilled water	6.4	25.4	23.5	20.0	400	0.91
MY4-02 <sup>2</sup>	distilled water	6.4	25.9	23.5	20.0	350	0.87
MY4-02	distilled water	9.1	25.2	23.0	16.0	400	0.96

oil sample	aqueous		IFT (mN/m)			$\tau$ (s)	$r^2$
	phase composition	pH	initial	initial	final		
			measured	fit			
MY4-02	distilled water	9.2	25.4	23.0	17.5	350	0.91
MY4-02	distilled water	10.7	nm				
MY4-02	SSW	6.4	21.5	20.0	13.0	300	0.96
P-VE-00	0.1M NaCl	3.1	16.1	17.5	16.4	120	0.79
P-VE-00	0.1M NaCl	5.2	23.3	22.5	21.0	100	0.54
P-VE-00	0.1M NaCl	6.4	23.8	23.0	20.8	150	0.71
P-VE-00	0.1M NaCl	8.9	19.0				
P-VE-00	0.1M NaCl	10.7	20.3	18.0	8.0	50	0.87
P-VE-00	distilled water	3.2	23.2	22.5	20.5	100	0.83
P-VE-00	distilled water	5.1	24.6	23.5	21.7	200	0.83
P-VE-00	distilled water	6.4	24.8	23.5	21.6	320	0.90
P-VE-00	distilled water	9.0	24.5	24.0	20.7	200	0.97
P-VE-00	distilled water	10.7	22.4	20.0	13.5	190	0.90
S-Ven-39	distilled water	6.4	20.8	22.5	20.6	200	0.63
S-Ven-39	SSW	6.4	20.7	20.6	18.2	400	0.87
S-Ven-40	distilled water	6.4	23.4	23.0	21.2	350	0.76
S-Ven-40	SSW	6.4	21.6	22.1	18.3	600	0.92
S-Ven-41	distilled water	6.4	24.6	22.5	20.6	250	0.75
S-Ven-41	SSW	6.4	20.5	21.6	18.8	500	0.79
S-Ven-41	SSW-HCO <sub>3</sub>	7.8	13.3	19.7	9.9	300	0.96
SQ-95	distilled water	3.2	23.8	23.5	22.0	120	0.60
SQ-95	distilled water	5.2	24.4	23.5	22.0	120	0.62
SQ-95	distilled water	6.5	24.3	23.0	20.0	120	0.62
SQ-95	distilled water	8.0	24.6	23.5	22.0	150	0.76
SQ-95	distilled water	9.0	24.0	23.0	12.0	160	0.97
SQ-95	distilled water	10.3	16.4	16.0	5.8	19	0.98
SQ-95	distilled water	10.9	8.0				
Tensleep-99	distilled water	3.5	21.0	19.5	15.5	330	0.98
Tensleep-99	distilled water	5.2	20.3	19.0	15.5	300	0.97
Tensleep-99	distilled water	6.5	20.5	19.0	15.0	280	0.96
Tensleep-99	distilled water	9.0	20.7	18.0	11.5	160	0.96
Tensleep-99	distilled water	11.0	15.5				
W-Br-03	distilled water	6.4	24.3	24.5	23.0	80	0.40
W-Br-03	SSW	6.4	17.6	23.8	20.0	350	0.90
W-Br-03	SSW-HCO <sub>3</sub>	7.8	20.9	22.8	11.4	300	0.98
W-Lo-03	distilled water	6.4	19.8	21.5	19.7	120	0.76

<sup>1</sup> SSW = synthetic sea water (see Table 1)

<sup>2</sup> duplicate measurements

<sup>3</sup> nm = not measureable

<sup>4</sup> SSW-HCO<sub>3</sub> = synthetic sea water recipe with sodium bicarbonate (see Table 1)