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Interfacial tension between oil and seawater as a function of dispersant dosage

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ABSTRACT

This paper presents a compilation of data describing interfacial tension between oil and seawater ($IFT_{(oil\text{-}water)}$) as a function of dispersant dosage. The data are from several earlier laboratory studies simulating subsea oil blowouts to evaluate subsea injection of dispersant (SSDI). Three dispersants were tested with four oil types to give a large variation in oil properties (paraffinic, light, waxy and asphaltenic). A general expression for $IFT_{(oil\text{-}water)}$ as a function of dispersant dosage is proposed based on the compiled data. $IFT_{(oil\text{-}water)}$ versus dosage is needed by algorithms to predict oil droplet sizes from subsea releases. However, such a relationship based on averaged data should be used with care and IFT measurements on the actual oil-dispersant combination should always be preferred.

1. Introduction

The subsea release of oil from the MC252 well in the Gulf of Mexico in 2010 was the first incident where subsea dispersant injection (SSDI) was used (Place et al., 2010). The amount of oil released subsea during the 87 day blow out was uncertain and estimates range from 35,000 to 75,000 bbl/day or 6000–12,000 m^3/day (Reddy et al., 2011; Ryerson et al., 2012). The total amount of dispersant injected subsurface was estimated to 3000 m^3 (Lehr et al., 2010).

When applied to a surface oil slick, dispersants are usually sprayed targeting a dosage of 4%. Even with this dosage, multiple applications can be needed to achieve sufficient effectiveness, if the dispersant is sprayed on a weathered oil with high viscosity due to emulsification (Daling et al., 1990). The surfactants in the dispersants have to break the oil-in-water emulsions and then disperse the oil (Daling et al., 2003). Using a 4% dosage with a large subsea release (7000 m^3/day) would require a stable supply of a substantial amount of dispersants (280 m^3/day), which would exhaust international stockpiles within a few days. However, experiments performed in earlier studies have shown that the dosages needed for SSDI are significantly lower compared to surface application (Brandvik et al., 2018). This reduced dosage could be explained by several factors. During SSDI, dispersant could be injected directly into the oil reducing loss and increasing dispersant-oil mixing, compared to spraying dispersants on weathered surface slick. The fresh, usually warm oil with low viscosity should also need less dispersant to disperse compared to a viscous emulsified surface oil. Finally, the energy available to disperse the oil is also significantly higher in a highly turbulent blow-out compared to wave induced turbulence at the surface.

This paper presents a compilation of data describing interfacial tension between oil and seawater ($IFT_{(oil\text{-}water)}$) as a function of dispersant dosage. The data are from several earlier laboratory studies simulating subsea oil blowouts to evaluate subsea injection of dispersant (SSDI). However, the majority of the data are from a study where three dispersants were tested with four oil types to give a large variation in oil properties. More details regarding the SSDI effectiveness studies are available from the technical reports and earlier publications (Brandvik et al., 2014, 2015, 2019). $IFT_{(oil\text{-}water)}$ versus dispersant dosage is important for most models used to describe fate and effect of subsea releases of oil and gas.

2. Experimental

2.1. SINTEF Tower Basin

The experiments described in this paper were performed in a Tower Basin at SINTEF in Trondheim, Norway, consisting of a 6 m high and 3 m wide basin containing 42,000 Litres of natural sea water. Oil was released from an orifice at the base of the basin and dispersant was injected into the oil as it was released. Measurements of the oil droplet sizes 2 m above the release point were used to quantify the effect of the dispersant injection. All experiments were performed with a 1.5 mm

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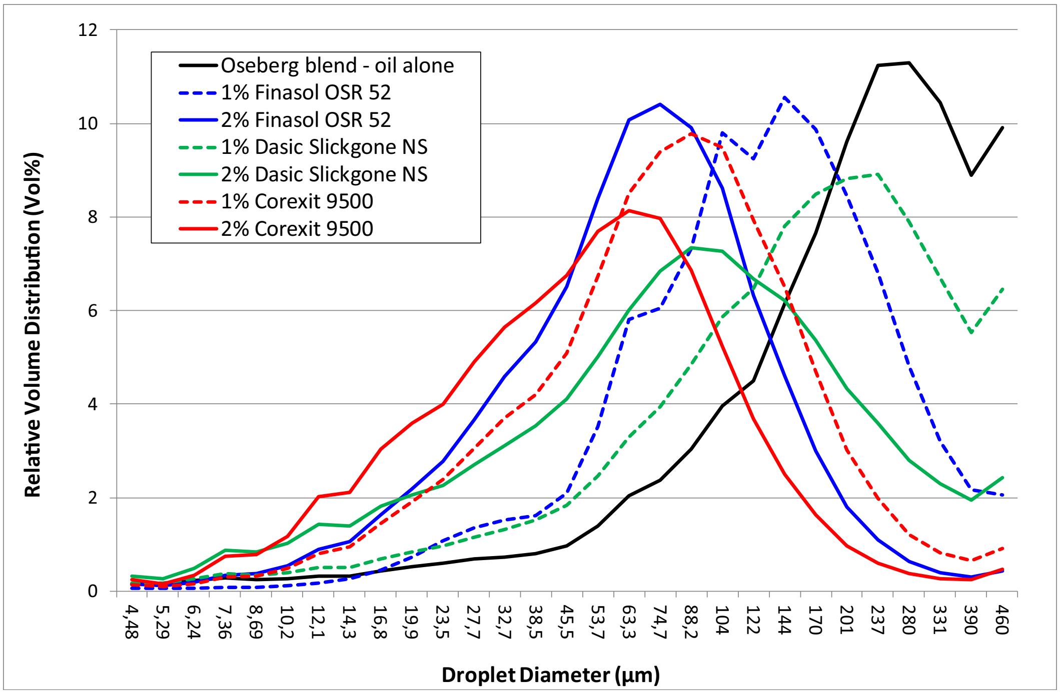

Fig. 1. Relative droplet size distribution (volume %) as a function of dispersant type and dosage (1% & 2%) with Oseberg blend. Release conditions 1.5 mm, 1.2 L/min and simulated injection tool (SIT) used for dispersant injection. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

nozzle, oil flow rate of 1.2 L/min, water temperature of 8–12 °C and oil temperature of 18–20 °C. The principles of the tower basin, oil release system and the instrumentation are described elsewhere (Brandvik et al., 2013).

The data presented in this study have been compiled from multiple experimental studies performed in the Tower Basin. Some of the studies focused on varying dispersant dosage (0.1% to 4%), others focused on different oil properties or different dispersant products. The longest series of experiments in the tank lasted for 15 min, injecting 15–20 l of oil and 150 ml of dispersant. Reference experiments (oil alone, no dispersant) were performed first and last in each series. Droplet size distributions and $IFT_{(oil\text{-}water)}$ for these reference experiments were compared to document the very low influence of the (increasing) background concentration of dispersant in the tank during a series of experiments. See the technical report for further details (Brandvik et al., 2015).

The effectiveness testing of the three dispersants and four oil types were performed by testing all oil types with one dispersant in one tower basin experiment, and then the sea water (42 m^3) in the tower basin had to be changed. This means that all oil types were tested multiple times and comparing droplet size distributions of untreated oils from experiments conducted over a period of three months give a good indication of the variability between experiments. Replicate experiments with Corexit 9500 and Oseberg crude are presented in the technical report (Brandvik et al., 2015) and show a good reproducibility during the experimental period.

2.2. Quantification of oil droplet sizes

Oil droplet sizes were quantified with a laser diffraction instrument (LISST 100X), providing a volume-based distribution of the diameter of oil droplets passing through its measurement chamber. The shift in droplets sizes was used to quantify the effect of the dispersant injection. The instrument makes 10 measurements every second (covering 32 logarithmic spaced bins in the 2.5–500 µm diameter range) and stores these as an average reading. An average over a 30 s period, which means 300 individual droplet size scans, was used in this study to quantify each droplet size distribution. Averaging over this period should reduce uncertainties from possible drifting or pulsing in oil or dispersant flow rates and inhomogeneity in the rising oil plume. If the droplet sizes are assumed to follow a lognormal distribution, the peak diameter will coincide with the volume median droplet size (VMD) or d_{50}. The peak of the distribution was for this reason used as an estimate for d_{50} in this study. More details on this issue are given in an earlier paper (Johansen et al., 2013).

2.3. Selection of oil types

The main parts of the experiments were performed with Oseberg blend, a crude oil with similar properties as the MC252 oil spilled during the Deep Water Horizon release in the Gulf of Mexico in 2010. They are both light paraffinic crudes with high evaporative loss and their weathering properties are characterized at SINTEF (Daling et al., 2014). Three other oil types have been added to span out a large variation in oil properties. The data describing the oils are from earlier oil weathering studies at SINTEF, describing the oil behavior when spilt at sea (Rist et al., 2010; Strøm, 2013; Moldestad and Rist, 2008; Leirvik and Resby, 2007).

These four oils represent a broad selection of oil types and should be representative for a large number of oils worldwide.

- Paraffinic crude oil (Oseberg): Rich in paraffins and saturated components, low density (or high API gravity) and moderate viscosity.
- Asphaltenic crude oil (Grane): Rich in polar resins and asphaltenes, high density (or low API gravity) and high viscosity.
- Light paraffinic oil (Kobbe): Contain mostly light hydrocarbons, low in polar resins, asphaltenes and waxes, low density (or high API gravity) and low viscosity.
- Waxy crude oil (Norne): Rich in waxes (higher saturated components > C20), high pour point, low density (or high API gravity) and moderate viscosity.

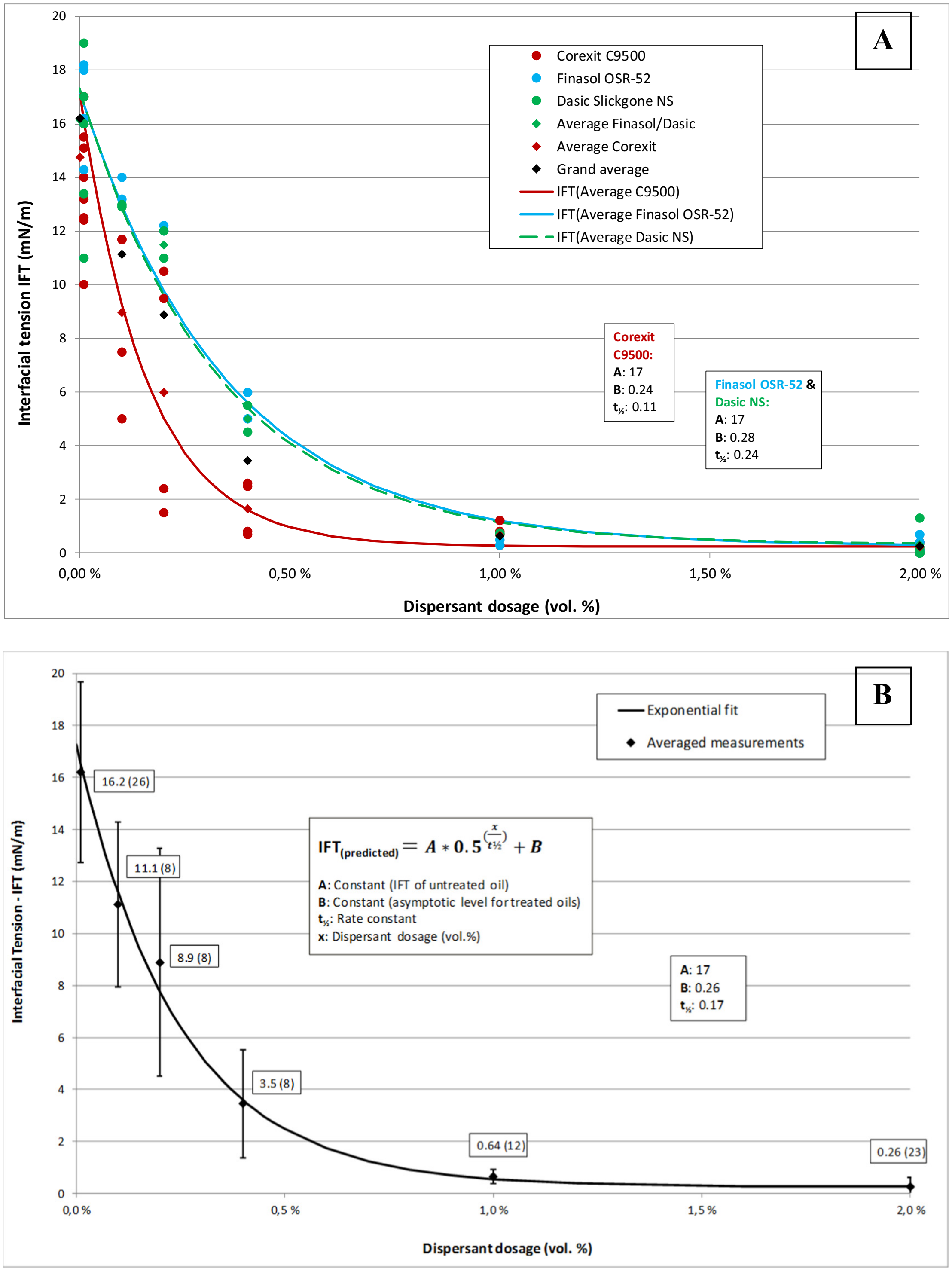

Fig. 2. Upper part: $IFT_{(oil\text{-}water)}$ as a function of dispersant type, dosage and oil type (A). Lower part: Averages for all oil types are represented by black diamonds. Equation is the best fit to the grand average of samples (B). Numbers in brackets are grand averages and number of measurements (n). Error bars are standard deviations. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

2.4. Selection of dispersants

Three commercial dispersants were included in this study; Corexit C9500, Finasol OSR 52 and Dasic Slickgone NS. They were supplied by Nalco in the US, Total Fluids in France and Dasic International in the UK and used as supplied.

2.5. Dispersant injection techniques

How the dispersant is injected into the oil influence the measured oil droplet size distribution. The effectiveness of different injection techniques was evaluated in a previous paper (Brandvik et al., 2018) and one injection technique from this study, simulated insertion tool (SIT), was used in the experiments presented in this study (Fig. 1). With SIT, the dispersant was injected into the oil stream 6 release diameters

Table 1
Oil properties for the four oil types used in this study.

	Oseberg blend (Paraffinic)	Grane (Asphaltenic)	Kobbe (Light paraffinic)	Norne blend (Waxy)
Density (kg/L)	0.832	0.941	0.797	0.860
Pour point (°C)	−6	−24	−36	21
Interfacial tension (mN/m)	17	11	15	20
Viscosity (mPa·s), shear rate 100 s^{-1}, 13 °C	9.6	593	5.3	40
Asphaltene (weight %)	0.3	1.4	0.03	0.3
Waxes (weight %)	3.2	3.2	3.4	4.2

before the release nozzle opening. The operational situation simulated by this injection technique could be dispersant being injected with a wand inserted 2.4 m (6 D) down into a pipe with a diameter of 0.4 m. Further details are given in Brandvik et al. (2018).

2.6. Interfacial tension

$IFT_{(oil\text{-}water)}$ was measured using the spinning drop method (Khelifa and So, 2009). For most of the experiments water samples containing dispersed oil droplets were sampled from the oil plume inside the tower basin during the experiment. The oil droplets were separated from the water, sampled, and stored for later IFT analysis. The oil droplets were left to rise and separate in a long-neck sampling bottle for 24 h. The long settling time was important since the smaller oil droplets could account for a large part of the interfacial area and must be included to get stable IFT measurement. All spinning drop analyses were performed at 13 °C with natural (3.5%) salt water. Measurements of droplets dimensions in the spinning drop instrument were taken as soon as the drop elongation was stable. In these studies, it is important to use the initial IFT measured 10–60 s after the oil droplets are stable in the instrument. The IFT could gradually decrease and readings after 30 min usually give significantly lower values. However, the initial oil droplet formation in a liquid jet released into stagnant water, is usually taking place within 4–6 release diameters from the nozzle opening (Or et al., 2011). In our Tower basin experiments this corresponds to less than a second, indicating that the initial IFT value is more significant for describing oil droplet formation in our experiments. The IFT measurements were done on multiple droplets and standard deviations were typical ± 0.2 for high IFT values (2–20 mN/m) and ± 0.01 for low IFT values (0.01–2 mN/m). Further details are given in Brandvik et al. (2013, 2018).

3. Results and discussions

Multiple oil types and dispersants have been tested in the Tower Basin and an example of these results is shown in Fig. 1. The figure presents droplet size distributions measured in-situ in the rising oil plume inside the tower basin. The black solid line presents the distribution of the large untreated oil droplets, while the smaller oil droplets created by injecting dispersant are presented by the colored dotted lines (1%) and colored solid lines (2%). The different colors represent the three dispersants (Corexit 9500, Finasol OSR-52 and Dasic Slickgone NS).

In Fig. 1, we interpret the reduction in droplet size, compared to the untreated oil, as a measure of dispersant effectiveness, simulating subsea dispersant injection (SSDI). We observe increased effectiveness (smaller droplets) for all three products, when dispersant dosage is increased from 1% (dotted lines) to 2% (solid lines). The figure also shows that the difference in performance between the three products is larger at lower dosage (1%) compared to injecting a higher dosage (2%). Corexit 9500 causes the larges reduction in oil droplet sizes at both dosages.

There are two main approaches for predicting oil droplet sizes in models used to describe the fate of oil from subsea blowouts.

1. Dynamic population models, which start with a large droplet size and model breakup and coalescence processes as a function of time conserving mass and momentum (e.g., Zhao et al., 2014, 2016; Nissanka and Yapa, 2016).
2. Equilibrium models, which predicts a stable droplet size distribution described by mean and standard deviation (e.g. Hinze, 1955; Johansen et al., 2013; Li et al., 2017).

The first approach could offer increased understanding and visualization of the dynamics during oil droplet formation, while the later only offers a distribution, but is computational very fast. One of these, called the modified Weber scaling, proposed by Johansen et al. (2013), is implemented in many models, both commercial and academic, describing subsea oil and gas releases (Socolofsky et al., 2015).

Both approaches, described above, use $IFT_{(oil\text{-}water)}$ as an important input describing oil droplet formation, especially to predict reduction in oil droplet sizes when dispersant is injected. Some data are available in the literature regarding $IFT_{(oil\text{-}water)}$ (e.g. Venkataraman et al., 2013), but data on different oil types, dispersant products and as a function of dispersant dosage are usually not readily available.

With a purpose of describing the relationship between IFT and dispersant dosage, data were compiled from several earlier studies (Brandvik et al., 2014, 2015, 2019). These studies cover IFT measurements both with premixed dispersants and with oil sampled during experiments in the Tower basin in varying dosages (0.01–4%). The compiled $IFT_{(oil\text{-}water)}$ data is presented in Fig. 2a–b and Table 2. The measured IFT shows a significant drop with increasing dispersant dosage for all three dispersants, with Corexit 9500 (red color in Fig. 2A) generally giving lower IFT values than the other two products (blue/green colors in Fig. 2A). The measured IFT values for Corexit 9500 with Oseberg are also very similar to those reported, with another light paraffinic crude (Louisiana sweet), by Venkataraman et al. (2013).

The grand average data in Fig. 2B can be used to express a general relationship for these three dispersants over a wide variety of oil properties. The exponential relationship between IFT and dispersant dosage (vol%) derived from the experiments with these oils and dispersants was:

$$IFT_{(oil-water)} = f(x, a, b, x½) = a0.5^{\left(\frac{x}{x½}\right)} + b \quad (1)$$

where a is a constant representing average IFT of untreated oil, b is a constant representing the average asymptotic level for treated oils, $x_{1/2}$ is the rate constant and x is the applied dispersant dosage (vol%). The average IFT for a 2% dosage is used as an estimate for b. The best exponential fit to the grand average of the experimental data (sum of least squares) was represented by: a = 17, b = 0.26 and a $x_{1/2}$ = 0.17 (black line in Fig. 2B). Similar lines for the individual dispersants are given in red (Corexit 9500), blue (Finasol OSR-52) and green (Dasic Slickgone NS). The best fit for exponential lines for the individual dispersants (Fig. 2B) have $x_{1/2}$ of; 0.11 and 0.24 (see colored lines in Fig. 2A).

However, there is a large scatter in the laboratory data behind the best fit Eq. (1), see error bars in Fig. 2B (standard deviation), and especially the equation for the individual dispersants, should be used with care. As an example, the asphaltenic Grane (see Table 1) was

Table 2
Measured interfacial tension ($IFT_{(oil\text{-}water)}$) as a function of dispersant dosage (0–4%) for four different oil types and three different dispersants. See legends at end of table. Data is also presented in Fig. 2.

Dosage (Vol.%)	IFT (mN/m)	Dispersant[1]	Oil[2]	Source[3]
0,0 %	13,2		1	A
0,1 %	11,7	1	1	A
0,2 %	9,5	1	1	A
0,4 %	2,6	1	1	A
1,0 %	1,2	1	1	A
2,0 %	0,08	1	1	A
4,0 %	0,05	1	1	A
0,0 %	15,1		1	A
0,1 %	5,0	1	1	A
0,2 %	1,5	1	1	A
0,4 %	0,8	1	1	A
1,0 %	0,3	1	1	A
2,0 %	0,008	1	1	A
4,0 %	0,07	1	1	A
0,0 %	15,5		1	A
1,0 %	0,8	1	1	A
0,0 %	12,4		1	A
2,0 %	0,03	1	1	A
2,0 %	0,03	1	1	A
0,0 %	17		1	B[1]
0,1 %	7,5	1	1	B[1]
0,2 %	2,4	1	1	B[1]
0,4 %	0,7	1	1	B[1]
1,0 %	0,3	1	1	B[1]
2,0 %	0,07	1	1	B[1]
4,0 %	0,05	1	1	B[1]
0,0 %	19		1	B[1]
0,1 %	13	2	1	B[1]
0,2 %	11,0	2	1	B[1]
0,4 %	4,5	2	1	B[2]
1,0 %	0,7	2	1	B[1]
2,0 %	0,2	2	1	B[1]
4,0 %	0,05	3	1	B[1]
0,0 %	18		1	B[1]
0,1 %	14	3	1	B[1]
0,2 %	12	3	1	B[1]
0,4 %	5,0	3	1	B[1]
1,0 %	0,50	3	1	B[1]
2,0 %	0,1	3	1	B[1]
4,0 %	0,12	3	1	B[2]
0,0 %	12,5		1	B
0,1 %	11,7	1	1	B
0,2 %	10,5	1	1	B
0,4 %	2,50	1	1	B
1,0 %	0,7	1	1	B
2,0 %	0,005	1	1	B
4,0 %	0,05	1	1	B
0,0 %	13,4		1	B
0,1 %	12,9	2	1	B
0,2 %	12,0	2	1	B
0,4 %	5,5	2	1	B
1,0 %	0,75	2	1	B
2,0 %	0,01	2	1	B
4,0 %	0,06	2	1	B
0,0 %	14,3		1	B
0,1 %	13,2	3	1	B
0,2 %	12,2	3	1	B
0,4 %	6,0	3	1	B
1,0 %	0,3	3	1	B
2,0 %	0,06	3	1	B
4,0 %	0,14	3	1	B
0,0 %	21,0		2	B
0,0 %	20,4		2	B
0,0 %	18,2		2	B
0,0 %	17,0		1	B
0,0 %	17,0		1	B
0,0 %	16,2		1	B
0,0 %	14,0		3	B
0,0 %	16,0		3	B
0,0 %	16,0		3	B
0,0 %	10,0		4	B
0,0 %	11,0		4	B
0,0 %	11,0		4	B
2,0 %	0,10	1	2	B
2,0 %	1,3	2	2	B
2,0 %	0,01	3	2	B
2,0 %	0,40	1	1	B
2,0 %	0,01	2	1	B
2,0 %	0,4	3	1	B
2,0 %	0,06	1	3	B
2,0 %	0,05	2	3	B
2,0 %	0,7	3	3	B
2,0 %	4,0	1	4	B
2,0 %	5,2	2	4	B
2,0 %	4,1	3	4	B
0,0 %	22,4		1	C
0,0 %	22,4		1	C
0,0 %	19,2		1	C
0,0 %	19,2	1	1	C
1,0 %	0,50	1	1	C
1,0 %	0,80	1	1	C
1,0 %	0,80	1	1	C
2,0 %	0,70	1	1	C
2,0 %	0,80	1	1	C
2,0 %	0,80	1	1	C
2,0 %	0,01	1	1	C

1) Dispersant: 1: Corexit 9500, 2: Finasol OSR52, 3: Dasic Slickgone NS.
2) Oil: 1: Oseberg blend, 2: Norne, 3: Kobbe. 4: Grane.
3) Source: A: Brandvik et al. (2014). B: Brandvik et al. (2015) and C: Brandvik et al. (2019). B[1]: Measured on samples where oil and dispersant were premixed in the lab. Not from Tower basin.
4) The measured IFT values for asphaltenic Grane were regarded as outliers and not included in Fig. 2.

regarded as an outlier and not included in the data for Fig. 2B. Experiments with this asphaltenic crude gave small oil droplets (see Brandvik et al., 2015 for details), with surprisingly high IFT values (4–5 mN/m), even at 2% dispersant dosage.

4. Conclusions

A general expression is proposed describing the interfacial tension between water and sea water ($IFT_{(oil\text{-}water)}$) as a function of dispersant dosage. This relationship is needed for most algorithms used to predict oil droplet sizes from subsea releases. However, laboratory measurements of IFT at relevant conditions should always be preferred, since some oils (in this study viscous asphaltenic oils), show significant deviations from the proposed relationship.

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