Application report

Application report:

Industry section: Cosmetics, Chemistry, Petroleum, Pharmaceutics

Authors: Ming Jin, Maria Mihhailova, Stefan Benn, Patrick Swolana, Daniel Frese

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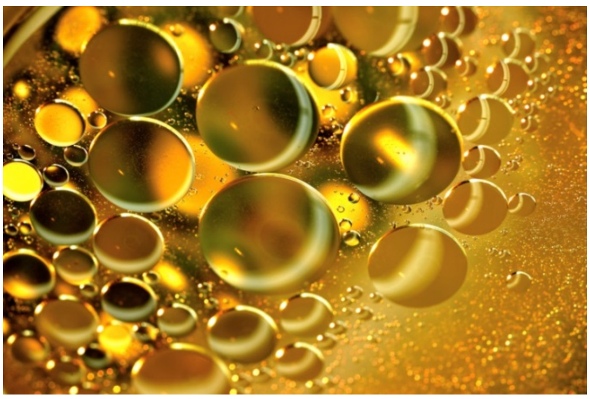
From an immiscible water-oil system to the ultralow interfacial tension of a microemulsion

Determining IFT in a range of six decades with one and the same instrument

In industrial applications such as enhanced oil recovery (EOR), pharmaceutics, or cosmetics, it is often necessary to mobilize and transport hydrophobic substances in aqueous media. The ideal way to do this is to form a microemulsion, i.e. a thermodynamically stable dispersion. When trying to synthesize such mixtures, the interfacial tension (IFT) between water and the hydrophobic phase can range from 50 mN/m for the raw substances to values as low as 10^{-5} mN/m for the fractions of a successfully created microemulsion. In search of just the right composition, it is helpful to use a measuring instrument that covers this very broad IFT spectrum.

In this Application Report, we first demonstrate how an impressively wide range of IFT can be measured by means of the Spinning Drop Tensiometer – SDT, starting with a simple system consisting of a water phase, an oil phase (cyclohexane) and a hydrotrope (*tert*-butyl alcohol). The measured values from 50 mN/m down to 0.1 mN/m are in good agreement with published data of a Force Tensiometer – K20 and even show a better reproducibility. By extending the analyses to a phase system of ultralow IFT, we could show that the instrument is capable of giving reliable results over a range of six decades, i.e. down to $2.7 \cdot 10^{-5}$ mN/m.



Background

Measuring IFT with the Spinning Drop Tensiometer – SDT

The Spinning Drop Tensiometer – SDT allows optical determination of liquid-liquid IFT by shape analysis of a drop of a light phase surrounded by a heavy phase [2]. The drop is elongated in a filled, rotating capillary due to the centrifugal force, which is counteracted by the IFT that forces the drop into a round shape. As a result, the IFT can be calculated by analyzing the curvature (with the Young-Laplace approach) or the vertical diameter of the elongated drop (Vonnegut approach).

Some strong points of the SDT as a state-of-the-art instrument are its patented capillary filling procedure and automatic drop launch function [3], the high degree of automation powered by the ADVANCE software, the precise image calibration with an integrated cone of defined dimensions, and the strobe light illumination for precise drop profile detection, just to name a few.

Influence of hydrotropes on water-oil IFT

Hydrotropes are small amphiphilic molecules that can increase the solubility of hydrophobic substances in water, thus acting as a cosolvent. Hydrotropes tend to decrease the IFT between water and oil phase, but, unlike surfactants, they don’t form stable micelles in water because the hydrophobic parts of their molecules are too small. They are commonly applied to enhance the stability of microemulsions. A typical example is *tert*-butyl alcohol (TBA).

Experimental section

A simple system consisting of double-distilled water as heavy phase and cyclohexane (CHX, Sigma Aldrich, anhydrous, ≥ 99.5 %) as light phase was investigated in terms of IFT with different fractions of TBA (Carl Roth, ≥ 99.5 %). All chemicals were used without further purification. The sample mixtures were prepared according to reference [1] and phases were saturated in each other. Density and IFT data as determined with a Force Tensiometer – K20 were taken from the same publication and are available as part of the supporting information [4]. Sample composition and literature data are listed in table 1.

IFT measurements were performed using a Spinning Drop Tensiometer – SDT. The temperature was controlled by a thermostat connected to the instrument and set to 20 °C.

Tab. 1: Composition and density of sample mixtures as taken from [1, 4].

Sample No.	Molar fraction TBA/water (eq.) [%]	Density light phase [g/cm^3]	Density heavy phase [g/cm^3]
1	0.00	0.776	0.998
2	0.11	0.778	0.998
3	0.88	0.776	0.992
4	3.77	0.776	0.976
5	5.54	0.783	0.971
6	6.52	0.802	0.966
7	7.91	0.835	0.953

Results

Fig. 1 shows exemplary drop images for the highest IFT (A, sample 1) and the lowest IFT (B, sample 7) of tested samples.

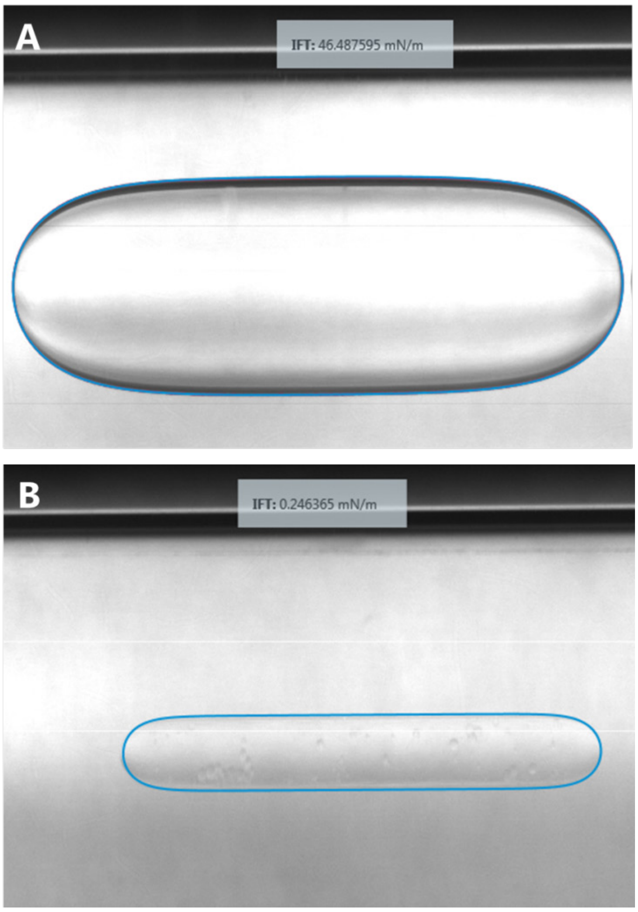


Fig. 1: Exemplary drop images of sample 1 (A) and sample 7 (B). The rotational speeds are 12000 and 6000 rpm, respectively. Drops were fitted according to Young-Laplace.

The resulting IFT values for all tested samples, as well as the data from literature that were measured using a K20 force tensiometer [1], are listed in table 2. Additionally, in fig. 2 the normalized IFT is plotted against the mol fraction of TBA in water for SDT and K20 for comparison. The data obtained from both methods are in good agreement, while especially for low IFT values, the standard deviation of SDT measurements is much lower than the one for K20 measurements. Actually, with 0.3 mN/m, the uncertainty for K20 Wilhelmy method is three times the measured IFT, which is why for low IFT values, the spinning drop method is clearly recommended over force-based methods.

Tab. 2: IFT values and standard deviation (N=3-4) determined with SDT (this study) and with K20 (Wilhelmy plate method, [1]) of sample mixtures. Standard uncertainty for Wilhelmy plate method is 0.3 mN/m according to [1].

Sample No.	IFT (SDT) [mN/m]	IFT (Wilhelmy plate method, K20), [mN/m], [1]
1	46.589 ± 0.096	48.8
2	41.740 ± 0.088	41.0
3	24.192 ± 0.037	24.5
4	7.731 ± 0.058	7.3
5	2.475 ± 0.004	2.3
6	1.026 ± 0.004	1.0
7	0.235 ± 0.009	0.1

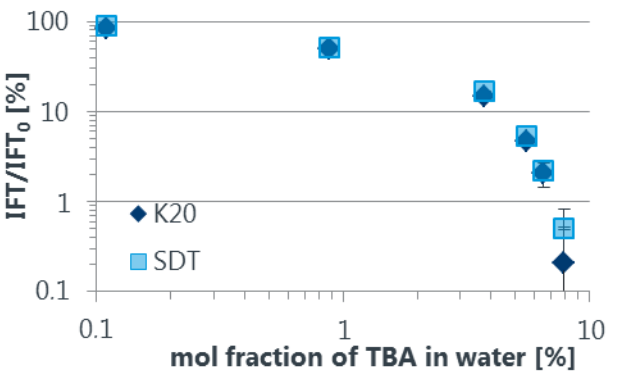


Fig. 2: Plot of normalized IFT (IFT divided by IFT of water vs. CHX without TBA = IFT$_0$) vs. molar fraction of TBA in water at equilibrium conditions. The data for spinning drop (light blue) and K20 (dark blue, [1]) overlap very well, while the standard deviation (error bars), especially for low IFT, is much smaller for SDT compared to K20.

In order to demonstrate the potential of the instrument in determining ultralow IFT, a mixture of water (250 mL), sodium chloride (25.5 mg), *n*-heptane (250 mL) and the surfactant AOT (dioctyl sodium sulfosuccinate, 55.5 mg) was prepared. This mixture has shown to give IFT values in the range of 10^{-5} mN/m [5]. All chemicals were thoroughly mixed, using a magnetic stirrer for 18 hours at room temperature. The mixture was filled into a separatory funnel. Separation into three phases occurred, which took about 4 hours.

The microemulsion center phase was used for the drop phase and measured against the aqueous bottom phase as the heavy phase with the SDT at 25 °C. An exemplary drop image together with the resulting IFT value of $2.7 \cdot 10^{-5}$ mN/m is shown in fig. 3.

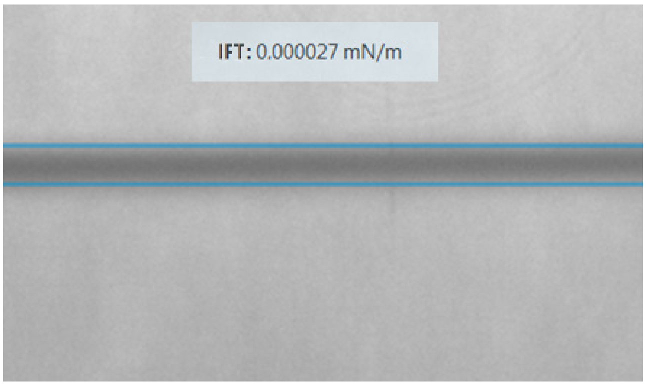


Fig. 3: Exemplary image of a drop of a microemulsion in the surrounding heavy aqueous phase for the system water-NaCl-*n*-heptane-AOT. The rotational speed was set to 1400 rpm. The drop was fitted according to Vonnegut.

Summary

To measure and control liquid-liquid interfacial tension (IFT) is of great importance for industries dealing with emulsions, especially microemulsions. We present IFT data that were recorded using a Spinning Drop Tensiometer – SDT for a simple system of water phase, oil phase, and cosolvent. The results match literature data very well while showing a much smaller uncertainty. For another microemulsion system, an IFT in the range of 10^{-5} mN/m was measured, underlining the very broad spectrum of IFT accessible with the SDT. This extensive range in combination with the user-friendly handling and advanced technical features for precise results make the SDT the instrument of choice for measuring low IFT values.

Literature

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