TITLE:

Accurate Determination of the Equilibrium Surface Tension Values with Area Perturbation Tests

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SUMMARY:

Two protocols for determining the equilibrium surface tension (EST) values using the emerging bubble method (EBM) and the spinning bubble method (SBM) are presented for a surfactant-containing aqueous phase against air.

ABSTRACT:

We demonstrate two robust protocols for determining the equilibrium surface tension (EST) values with area perturbation tests. The EST values should be indirectly determined from the dynamic surface tension (DST) values when surface tension (ST) values are at steady-state and stable against perturbations. The emerging bubble method (EBM) and the spinning bubble method (SBM) were chosen, because, with these methods, it is simple to introduce area perturbations while continuing dynamic tension measurements. Abrupt expansion or compression of an air bubble was used as a source of area perturbation for the EBM. For the SBM, changes in the rotation frequency of the sample solution were used to produce area perturbations. A Triton X-100 aqueous solution of a fixed concentration above its critical micelle concentration (CMC) was used as a model surfactant solution. The determined EST value of the model air/water interface from the EBM was 31.5 ± 0.1 $mN \cdot m^{-1}$ and that from the SBM was 30.8 ± 0.2 $mN \cdot m^{-1}$. The two protocols described in the article provide robust criteria for establishing the EST values.

INTRODUCTION:

The determination of the equilibrium surface tension (EST), or the equilibrium interfacial tension (EIFT), of a given air/water or oil/water interface is a critical step for applications in a wide range of industrial areas such as detergency, enhanced oil recovery, consumer products, and pharmaceutics[1–4]. Such tension values should be determined indirectly from the dynamic surface tension (DST) or the dynamic interfacial tension (DIFT), because only dynamic tension values are directly measurable. Dynamic surface tension values (i.e., measuring tension values as a function of time) are determined at regular time intervals. Equilibrium tension values are deemed to be determined when the DST values are at steady state. True equilibrium surface tension values are better established when they are stable against perturbations[5]. Several observations of the tension relaxation after surface area compression have been previously reported by Miller and Lunkenheimer, who used two classical tensiometry methods, the Du Noüy ring and the Wilhelmy plate methods[6–8]. Those methods are less accurate than the ones used in this study, and those DSTs were measured every few minutes. Numerous techniques have been developed for measuring the surface tension (ST) or interfacial tension (IFT) values of interfaces, but there are only a handful of techniques that can be used to measure DST or DIFT values and allow one to apply perturbations to test the stability of the acquired steady-state tension values[9]. If the aqueous solution contains surfactant mixtures, and when one of the components adsorbs much faster than the others, then there may be a temporary plateau in the DST curves[10]. Then the presented methods may not work well in the short time-scales as for one component surfactants, but they still may work if the procedures are extended slightly to cover longer time-scales.

The protocols described here show representative data only for surface tension values of an air/aqueous solution. However, these protocols also apply for the IFT of an aqueous solution against a second liquid, such as an oil, which is immiscible with the aqueous solution and has a smaller density than that of the aqueous solution. Here, we present two robust methods that satisfy these criteria, the emerging bubble method (EBM) and the spinning bubble method (SBM). In both methods, one determines ST values that are based on bubble shapes and do not require contact angle information, which can introduce significant uncertainties and errors to the measurements. For the EBM, area perturbations are introduced by abruptly changing the volume of the bubble emerging from a syringe needle tip. For the SBM, changes in the rotation frequency of the samples are used for area perturbations. The detailed protocols are aimed to guide researchers in the field, such that they can avoid common mistakes or errors in dynamic and equilibrium tensiometry and help prevent inaccurate interpretations of the acquired data.

PROTOCOL:

1. Minimum Instrument Specifications

1.1. Prepare a tensiometer for the EBM with the following specifications: (i) a dispensing system for controlling the dispensing gas volume; (ii) a camera for capturing the bubble image; (iii) image analysis software for solving the Laplace-Young equation (LY equation) with the axisymmetric bubble shape analysis algorithm[11, 12] (iv) a temperature-controlled sample chamber.

NOTE: Usually, the instrument for the EBM can also be used for the pendant drop method, in which a small drop is formed and hangs vertically from the end of a syringe needle.

1.2. Prepare a tensiometer for the SBM with the following specifications: (i) a sample tube holder that is capable of spinning a sample tube holder horizontally at high rotation frequencies of at least 6,000 rpm; (ii) a camera for capturing the image of the spinning bubble in the tube; and (iii) image analysis software to solve the general LY equation and Vonnegut equation[13].

NOTE: The protocol can be paused here.

2. Materials and Sample Preparation

2.1. Obtain pure water from a water purification apparatus. The resistivity of the water at 25 °C at the device output should be 18.2 MΩ·cm or close to it.

2.2. Clean all borosilicate vials, quartz cells, glassware, and magnetic stirring bars by soaking them in pure water for at least 8 h and repeat the soaking process at least one more time.

NOTE: the soaking process is aimed at removing residual ions from the glass containers, which can affect the surface tension values significantly.

2.3. Prepare a surfactant solution of interest in the cleaned glassware.

NOTE: The surfactant concentration should be lower than its solubility limit in the water.

2.4. Wash each container that will be used for the tension measurements with the sample solution that will be used for the actual measurements prior to sample loading.

2.5. Measure the densities of the liquid samples prior to the tension measurement to three or four significant figures.

NOTE: The protocol can be paused here.

3. Surface Tensiometry with the Emerging Bubble Method (EBM)

3.1. Calibrate the image-acquiring device of the tensiometer according to the vendor's user manual.

NOTE: The protocol can be paused here.

3.2. Select an inverted stainless-steel needle based on the estimated maximum bubble diameter from the estimated surface tension values.

NOTE: the maximum bubble diameter can be estimated from the capillary length, d_c ($d_c = \sqrt{(2\gamma/\Delta\rho g)}$, where γ is the surface tension ($N \cdot m^{-1}$), $\Delta\rho$ is the density difference of the liquid phase and the air ($kg \cdot m^{-3}$), and g is the gravitational acceleration ($m^2 \cdot s^{-1}$)). The maximum bubble volume (V_{max}) can be estimated as $\pi d_c^3/6$.

NOTE: The protocol can be paused here.

3.3. Place the inverted stainless-steel needle, obtained from the same vendor of the tensiometer, at the tip of the dispensing device.

NOTE: An automated dispenser is recommended compared to a manual syringe, because it is easier and more accurate for the users to produce the desired volume, and then, volume and area perturbations to the surface. The smallest volume step of the dispenser is recommended to be less than 1 µL, from 0.2-0.5 µL, in order to produce precise area perturbations.

NOTE: The protocol can be paused here.

3.4. Determine the volume of the liquid sample for the tension measurements such that the depth of the liquid sample is long enough to have the entire inverted part of the dispensing needle submerged, and to have an additional ~20 mm depth of liquid sample between the inverted needle tip and the liquid sample surface.

3.5. Load a liquid sample in the quartz cell and place the cell on top of the sample platform. In our example, the liquid sample volume was 40 mL.

3.6. Adjust the height of the inverted needle such that the tip of the needle is at least 20 mm below the surface of the liquid sample.

3.7. Adjust the position of the inverted needle such that the boundary of the needle tip is parallel to the liquid-air surface.

3.8. Inject ~1 mL of air through the submerged inverted needle to remove impurities that could possibly be present on the tip of the syringe. This procedure is used to improve the surface chemical purity of the air/liquid interface.

3.9. Estimate the maximum bubble volume (V_{max}) with a procedure described as follows. First, dispense ~2 µL of air to form a bubble at the tip of the syringe and observe the bubble shape. Then, increase the bubble volume by ~0.5 µL and observe the bubble shape. Repeat the two previous steps until the bubble detaches from the needle tip. This step specifies the V_{max}.

3.10. Determine the appropriate range of the bubble volume, based on the previous set of observations.

NOTE: The bubble shape should be non-spherical, substantially deformed by gravity, to allow accurate use of the axisymmetric drop shape analysis algorithm, and the bubble volume should be quite smaller than the V_{max} to avoid bubble detachment from the needle tip. For the syringe tip with the inner diameter of 0.84 mm, the preferred initial bubble volume is about 4 µL.

3.11. Determine the initial bubble volume based on the bubble volume range determined from the previous step. The initial bubble volume should be close to the middle of the bubble volume range so that the volume, and area, perturbations produce bubbles inside the range.

3.12. Dispense the predetermined initial bubble volume from the previous step to form a bubble at the tip of the inverted syringe tip. Make sure that the bubble is in hydrostatic equilibrium, which means that the surface tension forces balance the gravity (buoyancy) forces.

NOTE: It is important to have the bubble pinned outside of the needle tip perimeter to prevent the presence of surfactant solution inside the syringe needle. If the bubble is pinned inside of the needle tip, repeat the protocol 3.7 to purify the needle tip.

3.13. Measure the dynamic surface tension based on the shape of the produced air bubble at the tip of the needle tip every 1 s, or another predetermined time interval. The recommended numerical algorithm for calculating surface tension is one based on the axisymmetric drop shape analysis method of the LY equation.[11, 12]

3.14. Compare the actual shape of the bubble with the calculated shape. If the two shapes overlap completely, or nearly, one infers that the equilibrium LY equation is valid for each dynamic and slowly-varying shape. This inference is completely valid when the bubble stops moving, and the ST stops changing, to have hydrostatic equilibrium.

NOTE: The criterion that the surface tension value is uniform throughout the interface and that hydrodynamic effects are not important is that the calculated bubble interface shape based on the optimal inferred surface tension values overlaps visually with the actual bubble interface shape. More quantitative tests are possible but will not be considered in this article.

3.15. Measure the surface tension as a function of time until the first steady-state surface tension (SST_1) is achieved. The SST is defined as a plateau value beyond which the surface tension changes by less than 1 $mN \cdot m^{-1}$ (or by less than 5%) in several (10 to 100) consecutive dynamic surface tension measurements.

3.16. Record the bubble volume (V_1) and the surface area (A_1)

3.17. Decrease the bubble volume by removing ~1 µL of air, and record the new bubble volume, V_2 and area, A_2 (see Figure 1).

3.18. Continue measuring the DST and the areas until the DST reaches the second SST (SST_2) at the bubble volume of V_2.

3.19. Expand the bubble volume by injecting ~1 µL of air so that $V_3 \approx V_1$ and $A_3 \approx A_2$.

NOTE: Having V_3 and A_3 exactly equal to V_1 and A_1 is not essential.

3.20. Continue measuring DST values until a third SST (SST_3) is reached. If the three SST values differ from each other by less than 1.0 $mN \cdot m^{-1}$, or by 5%, then their average is defined as the equilibrium surface tension (EST).

NOTE: The protocol can be paused here.

4. Surface Tensiometry with the Spinning Bubble Method (SBM)

4.1. Calibrate the image-acquiring device of the tensiometer according to the vendor's user manual.

NOTE: The protocol can be paused here.

4.2. Fill the glass tube of the sample holder, compatible with the spinning tensiometer for the measurement, with a liquid sample and close the lid. No air bubbles should be present inside of the glass tube.

NOTE: It is recommended that the sample holder and the glass tube, which are provided by the instrument vendor or are compatible with the tensiometer, be used.

4.3. Place the filled sample holder inside of the spinning chamber of the spinning tensiometer.

NOTE: The protocol can be paused here.

4.4. Spin the tube at a low rate of ~500 rpm to prevent the injected bubble from migrating upward and/or attaching to the tube wall.

NOTE: The protocol can be paused here.

4.5. Load ~2.0 µL of air in the syringe.

NOTE: The protocol can be paused here.

4.6. Insert the syringe needle piercing through the polymeric septum sealing the top of the spinning tube.

4.7. Inject an air bubble of ~2.0 µL into the spinning tube.

NOTE: The bubble volume usually remains constant, unless the bubble breaks. If the bubble breaks, it is better to start the process again.

4.8. Increase the rotation frequency of the sample holder to v_1 so the bubble inside the glass tube is deformed such that the ratio of the horizontal bubble length (L) and the radius of the middle of the bubble (R) to reach a value of 8 or greater.

NOTE: If, with the available instrument, the sample tube cannot be spun at a sufficiently high rotation frequency to allow substantial bubble deformation and have a L/R ratio of 8 or greater, the general LY equation can be used to calculate DST values.

4.9. Adjust the tilt angle of the measuring chamber containing the tube, if necessary, to position the sample tube oriented horizontally, to prevent bubble movement, and to help achieve gyrostatic equilibrium (hydrostatic equilibrium in a rotating fluid) for an axisymmetric shape assumed in the LY equation and algorithm used.

NOTE: Gyrostatic equilibrium is defined for rotating bubbles, analogously to the hydrostatic equilibrium of non-rotating bubbles, when the bubble is not moving.

4.10. Measure the dynamic surface tension (DST) values at a predetermined time interval. The typical value is 1 s.

4.11. Continue to measure the DST at a fixed rotation frequency, v_1, until it reaches a steady-state value (SST_1) and record SST_1 and the rotation frequency v_1 (see Figure 2).

4.12. Record the bubble volume, V_1 and area, A_1.

4.13. Alter the rotation frequency to a second rotation frequency, v_2, to vary the surface area.

4.14. Continue to measure the DST at a fixed rotation frequency, v_2, until it reaches a second steady-state value (SST_2) and the rotation frequency v_2.

4.15. Record the bubble volume, V_2 and area, A_2.

NOTE: V_2 should be very close to V_1.

4.16. Change the rotation frequency to v_3.

NOTE: Having v_3 exactly equal to v_1 is not essential.

4.17. Measure DST values at a fixed rotation frequency, v_3, until the third steady-state value, SST_3, is reached.

4.18. Record v_3 and A_3.

4.19. When the three SST values differ from each other by less than 1.0 $mN \cdot m^{-1}$ (or by less than 5%), their average is taken to be the “EST”.

REPRESENTATIVE RESULTS:

Dynamic Surface Tension and Equilibrium Surface Tension of an Aqueous Triton X-100 Solution with the Emerging Bubble Method

The SST values of the Triton X-100 solutions against air were measured, and their stability was tested for 5 mM aqueous solution; the CMC for this surfactant in water is 0.23 mM[14]. The SST_1, 31.5 ± 0.1 $mN\cdot m^{-1}$, was obtained approximately 20 s after the bubble was formed (Figure 3). After about 25 s, the surface area was compressed from A_1 = 11.4 mm^2 to A_2 = 9.0 mm^2 by reducing the bubble volume from V_1 = 3.8 µL to V_2 = 2.8 µL. The DST first dropped to 31 $mN\cdot m^{-1}$, and within 1 s, it increased to the SST_2 of 31.5 ± 0.1 $mN\cdot m^{-1}$. After about 50 s, the surface area was expanded abruptly from A_2 = 9.0 mm^2 to A_3 = 11.4 mm^2 by increasing the bubble volume from 2.8 µL (V_2) to 3.8 µL (V_3). The DST value changed little and hence, the SST_3 was determined to be 31.5 ± 0.1 $mN\cdot m^{-1}$. The three SST values were about the same. Therefore, the EST was determined to be 31.5 ± 0.1 $mN\cdot m^{-1}$.

Dynamic Surface Tension and Equilibrium Surface Tension of an Aqueous Triton X-100 Solution with the Spinning Bubble Method

At 9,000 rpm, the SST_1, 30.9 ± 0.1 $mN\cdot m^{-1}$, of the same Triton X-100 solution as that described above was reached about 500 s after the bubble was injected (Figure 4). Then the surface area was reduced by abruptly changing the rotation frequency from v_1 = 9,000 rpm to v_2 = 8,500 rpm. Then, the DST was decreased to 27.5 $mN\cdot m^{-1}$, and then within 1 s rose to 30.6 $mN\cdot m^{-1}$. Hence, the SST_2 was 30.6 ± 0.1 $mN\cdot m^{-1}$. After ~630 s, the surface area was expanded by increasing the rotation frequency from v_2 = 8,500 rpm to v_3 = 9,000 rpm. The DST jumped to ~34 $mN\cdot m^{-1}$, and then it decreased rapidly to a steady-state value of 30.8 ± 0.1 $mN\cdot m^{-1}$, the SST_3. Hence, the EST was determined as 30.8 ± 0.2 $mN\cdot m^{-1}$. The 2.2% difference in EST values from the two methods is probably due to certain systematic error; the discussion of these errors is beyond the scope of the current paper.

FIGURE AND TABLE LEGENDS:

Figure 1. Schematic diagram of dynamic surface tension (DST), steady-state surface tension values (SST_1, SST_2, and SST_3), and equilibrium surface tension (EST) with the emerging bubble method (EBM). V_1 is the initial bubble volume, and V_2 and V_3 are the bubble volumes after the first and the second volume, and area, perturbations, respectively.

Figure 2. Schematic diagram of dynamic surface tension (DST), steady-state surface tension values (SST_1, SST_2, and SST_3), and equilibrium surface tension (EST) with the spinning bubble method (SBM). Here, v_1 is the rotation frequency prior to area perturbations, and v_2 and v_3 are the rotation frequencies after the first and the second frequency, and area, perturbations, respectively.

Figure 3. Dynamic Surface Tension (DST) of the model surfactant in DI water (5 mM) against air with the emerging bubble method (EBM). In this figure, V_1 is the initial bubble volume, and V_2 and V_3 are the bubble volumes after the first and the second volume, and area, perturbations, respectively. Prior to each perturbation, the dynamic surface tension (DST) values reached a plateau value, which is defined as the steady-state surface tension (SST).

Figure 4. Dynamic Surface Tension (DST) of the model surfactant in DI water (5 mM) against air evaluated with the spinning bubble method (SBM). In this figure, v_1 is the rotation frequency prior to area perturbations, and v_2 and v_3 are the rotation frequencies after the first and the second frequency, and area, perturbations, respectively. Similarly to the EBM method, prior to each perturbation, the dynamic surface tension (DST) values reached a plateau value, which is defined as the steady-state surface tension (SST).

DISCUSSION:

The Emerging Bubble Method (EBM) and the Spinning Bubble Method (SBM) are simple and robust methods for determining tension values for air/water or oil/water interfaces at atmospheric pressure. Prerequisite information for these methods is the density of each phase, and no contact angle information is required for determining tension values[9]. A major limitation of the techniques is that the samples should have a low viscosity, and be single-phase or below the surfactant solubility. The two protocols, the EBM and the SBM, are used for measuring dynamic surface tension (DST) values to monitor them as a function of time. When a steady-state surface tension (SST) value is reached, the stability of the SST value is tested by measuring the DST after applying area perturbations. Then, unstable or metastable SST values can be screened out[5], and reliable equilibrium surface tension (EST) values can be determined.

The critical steps of the EBM protocol are (i) the removal of impurities from the syringe needle tip (Step 3.8) and (ii) the choice of a proper extent of each area perturbation. If the syringe needle tip contains surface-active impurities, the measured DST values may have significant errors compared to the ones with a purified tip. By forming and detaching a series of air bubbles at the syringe tip, surface-active impurities can be removed with the air bubbles. In addition, if the EST values have been found to vary significantly from bubble to bubble, it is recommended to begin the experiment with a new liquid sample and with properly-washed liquid sample containers and syringe needles. The washing process for the liquid containers is described in Step 2.2 and the same procedure can be used, if needed, for washing the syringe needles. Moreover, if the surface area has been compressed so much that the shape of the air bubble becomes close to a spherical shape, the resulting DST values may have significant errors due to the difficulties in obtaining accurate solutions with the available software. In such cases, the extent of area compression should be smaller, or the initial bubble volume, prior to the surface area compression, should be larger.

The critical steps of the SBM protocol are (i) injecting an air bubble without any intrusion of air bubbles and (ii) preventing the injected air bubble from contacting any solid surfaces (e.g., sample tube's inner wall or septum), such that the gyrostatic equilibrium can be maintained throughout each measurement. If multiple air bubbles are injected or formed in the spinning sample glass tube, and if those bubble are in close proximity to one another, then the resulting DST values may have significant errors due to hydrodynamic interactions between air bubbles. In such cases, it is recommended to begin the experiment again from the surfactant solution loading step (Step 4.2). Also, in order to maintain gyrostatic equilibrium throughout a measurement, it is highly recommended to keep monitoring the location of the spinning air bubble. Any drifting of the spinning bubble to either the left or the right direction can be minimized by controlling the tilt angle of the spinning sample holder.

The same tensiometer used for the EBM protocol can be also used for a pendant drop method configuration where the surfactant solution is suspended vertically at the end of the syringe tip. The pendant drop method has a disadvantage, relative to the EBM for the experiments requiring long times (over than about an hour), as the drop volume may decrease due to solvent evaporation. The pendant drop method may be preferred, however, when the available liquid sample volume is smaller than the minimum volume required for the EBM. The SBM method has certain advantages over the pendant drop method, the Du Noüy Ring method, or the Wilhelmy plate method because the sample is in a sealed tube throughout the measurements, thereby eliminating errors due to any solvent evaporation. In addition, as described in the introduction section, interfacial tensions (IFTs) between two immiscible liquids, such as oil and water for enhanced oil recovery applications[5, 15] or hydrocarbon and fluorocarbon for firefighting fluids[16], can be determined with the same tensiometers and with the same protocols.

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The authors have nothing to disclose.

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