

An Evaluation of Goniometric Methods

A Contribution from the Hematology at Biomaterial Interfaces Research Group

By

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1. Introduction

Investigators seeking to apply standard tools of contact angle and wettability (tensiometry) in studies of surface phenomena are frequently confronted with a hard choice among a variety of techniques and instrumentation vendors. Among the many tensiometric methods that have been developed over the years, contact angle goniometry and Wilhelmy balance tensiometry have become the standard and most popular methods (see refs. 1-3 and citations therein). In goniometry, a back-light drop (silhouette) is optically imaged and the angle subtended by the drop at the point of solid-liquid contact (on left and right sides) estimated with an optical goniometer (manual) or by image analysis (computerized). Wilhelmy balance tensiometry measures wetting forces along the perimeter of a regularly-shaped object (typically a plate or cylinder) as it is immersed into or emerged from the wetting liquid (see ref. 2 for a brief tutorial). Modern computerized instrumentation has greatly reduced labor and subjectivity of goniometric and balance techniques, but there are a number of analytical subtleties that can be easily overlooked in instrument setup and operation. For example, in goniometry, it is essential to establish an accurate baseline between the drop and surface and choose the correct point of contact. These two aspects are intertwined and both require that the observer must be looking down on the drop at a slight angle above (not below) the horizon. Otherwise, the base of the drop can be cropped by the horizon and finding the maximum profile width becomes highly ambiguous. In Wilhelmy balance tensiometry (WBT), buoyancy correction requires accurate knowledge of the wetted perimeter and point of liquid-plate contact; both of which insist that the test plate or cylinder enter and exit the fluid perpendicularly.

Measurement of advancing and receding contact angles, θ_a and θ_r , respectively, is an essential aspect of tensiometry because these are the two reproducible angles that characterize wetting. No doubt WBT is the most accurate and least subjective approach to measuring hysteresis ($\Delta = \theta_a - \theta_r$) because the three-phase (solid-liquid-vapor) line is in wholesale motion, assuring achievement of maximal θ_a and minimum θ_r . As a consequence, WBT is a reasonable choice as a benchmark of comparison for goniometric methods.³ Two goniometric methods widely applied in commercial instruments to measure θ_a and θ_r are the captive-drop (CDG) and tilting plate (TPG) goniometric techniques. In CDG, a drop is held in place on a surface under study with a fine needle connected to a syringe. Advancing angles θ_a are read by slightly filling the drop, advancing liquid over the surface. Receding angles θ_r are read by removing liquid from the drop, receding liquid from the surface. Maximum θ_a and minimum θ_r is assured by incrementally increasing volume added or removed, respectively, until no change in angles is observed. Care must be taken with CDG to use a needle diameter that is a very small portion of the drop diameter. We have found that if the needle diameter exceeds a few tens of microns, drop shape can be significantly affected and introduce serious errors into the estimation of θ_a and θ_r . TPG measures left and right sides of a drop as the surface under study is tilted with respect to the optical axis so fluid accumulates in the leading (advancing) edge of the drop and drains from the trailing (receding) edge. Maximum θ_a and minimum θ_r are attained when the drop is at a point of ‘incipient motion’; that is, just at the point when the drop rolls out of the observation window. Needless to say, finding the point of incipient motion is experimentally inconvenient. A typical remedy for a particular surface under investigation is to plot observed contact angle against tilt angle to find a tilt smaller than required to induce drop rolling yet large

enough that an incremental increase or decrease in tilt does not observably change left-and-right angles. Thus, finding maximal θ_a and minimum θ_r is yet another subtlety of the goniometric methods that warrants verification against WBT for stringent work.

Lander *et. al.*³ systematically compared hysteresis measured by CDG and TPG to WBT using a hexadecylsilane-coated glass and silicon wafers as a model surface. Using a multiplicity of similarly-prepared surfaces and hundreds of contact angle measurements, Lander found that WBT and TPG gave statistically-identical results whereas CDG consistently underestimated θ_a and over estimated θ_r . This paper expands on the work of Lander *et. al.* by comparing CDG and TPG hysteresis measurements to WBT using a variety of surfaces spanning a broad range of water wettability. We find good agreement among CDG, TPG, and WBT in measured advancing angles θ_a , corroborating Lander's results. However, in contrast to Lander's findings, receding contact angles θ_r measured by both CDG and TPG were found to be systematically offset from that of WBT and were highly variable relative to θ_a measurements. Thus, this work recommends neither CDG nor TPG for accurate measurement of receding contact angles or contact angle hysteresis.

2. Results and Discussion

Table 1 collects advancing (θ_a) and receding (θ_r) contact angles of water on silane-treated and surface-modified, silane-treated glass coverslips with varying water-wettability created for the purpose of comparing goniometric techniques (see Materials and Methods). Fig. 1 compares goniometry (TPG and CDG) to WBT where data falling along the diagonal corresponds to

perfect agreement among techniques. Inspection of the data trends reveal that θ_a measured by goniometric methods were in close agreement with WBT (and therefore regarded accurate) but θ_r was more noisy and systematically offset from WBT (and therefore regarded not accurate).

We attribute failure to achieve a stable lower-bound θ_r to a three-phase-line-pinning phenomenon⁴⁻⁶ that requires wholesale drop motion to overcome energetic barriers to formation of a uniform drop perimeter.

3. Conclusions

No single contact angle adequately characterizes wettability of a surface. Instead, a maximal advancing angle θ_a and minimum receding angle θ_r are required, with a range of metastable contact angles observable between these two bounds. An important question that arises in detailed analysis of contact angles and in choice among contact angle methods asks which technique offers the most accurate and precise measures of contact angle hysteresis.

Comparison of θ_a measured by tilting-plate goniometry (TPG) and the popular captive drop goniometry (CDG) to Wilhelmy balance tensiometry (WBT) confirms statistical agreement among methods for θ_a . However, θ_r measurements by TPG and CDG were systematically offset from the benchmark WBT and exhibited greater variability.

4. Experimental Section

Surfaces: Glass cover slips (Fisher Brand 22 x 30 x 0.1 mm) were used as substrates for the comparative analysis of contact angle measurements between tilting-plate goniometry (TPG), captive-drop goniometry (CDG) and Wilhelmy-balance tensiometry (WBT). As-received slides were cleaned by 3X sequential rinses in each of water, isopropanol and chloroform, and plasma-

discharge treated for ~5min in a Harrick Plasma cleaner (Ossining, NY) at 100 mTorr air. Distilled-deionized (18.2 M Ω -cm) water was used as test-solution for contact angle measurements. Surfaces of varying water wettability ($50^\circ < \theta_a < 120^\circ$) were prepared by silanization of clean glass cover slips (substrates). Three kinds of hydrophobic surfaces were prepared using (i) octadecyltrichlorosilane (OTS; $\theta_a \sim 110^\circ$), (ii) aminopropyltriethoxysilane (APTES; $\theta_a \sim 70^\circ$) and (iii) 0.2% solution of 1, 1, pentadecafluorooctylmethacrylate in trichlorotrifluoroethane (NYEBAR; $\theta_a \sim 120^\circ$; commercial fluorocarbon polymer coating fluid; Nye Lubricants, Fairhaven MA). Clean glass coverslips were silanated by a 2 hr reaction with 5% OTS in chloroform or 5 min reaction with 2% APTES. Silanated glass slides were 3X rinsed in chloroform (OTS) or acetone (APTES) before being cured in a vacuum oven at 110°C for 24 hr to ensure stable surface chemistry. NYEBAR surfaces were prepared by immersing OTS surfaces in NYEBAR solution for about 10 min with subsequent air-drying. Surfaces with incrementally-increasing wettability ($90^\circ > \theta_a > 45^\circ$) were prepared by chemical oxidation of OTS surfaces. Cured OTS surfaces were immersed at 5-minute intervals in 50% solution of H₂SO₄/Cr₂O₃ in water, followed by 3X sequential wash in ethanol, and air drying.

Tensiometry: Wilhelmy-balance tensiometry (WBT) was performed using a commercial computer-controlled instrument (Camtel CDCA 100, Royston UK) using solvent-and-plasma-discharge-cleaned glass coverslips as the plate. The balance was calibrated with standard weights thereby accounting for local variation in the force of gravity. No attempt was made to thermostat the balance and all reported measurements were made at ambient laboratory temperature. Also, no attempt was made to correct for the (presumably small but not measured) variation in the perimeter of the glass coverslips. Solutions (approximately 10 mL) were

contained in disposable polystyrene beakers (Fisher) previously determined not to measurably affect interfacial tension of water contained therein. Advancing and receding contact angles were calculated from the last of three immersion and emersion force measurements respectively, using a force-balance equation corrected for buoyancy (by extrapolation to zero volume);

$f = p\gamma_{lv} \cos \theta$; where f is the force in mN, γ_{lv} is the surface tension of water at 71.9 mN/m at 25 °C, p is the perimeter (wetted length) of the glass coverslip (44.2mm, for a thickness of 0.1mm) and θ is either advancing (θ_a) or receding (θ_r) contact angle.

Goniometry: Tilting-plate goniometry (TPG) was performed using a commercial-automated goniometer (First Ten Angstroms Inc., Portsmouth, VA). The tilting-plate goniometer (TPG) employed a Tecan liquid-handling robot to aspirate 12 μ L of water contained in a 96-well microtiter plate. The robot was used to reproducibly transfer the tip with fluid contents into a humidified (99+ % RH) analysis chamber and dispense 10 μ L drops onto the surface of test substrata (see below) held within the focal plane of a magnifying camera. These and all other aspects of TPG were performed under computer control. Proprietary algorithms supplied by the vendor were used to deduce contact angles from drop images captured at a programmed rate by a frame grabber. Typically, 300 images were captured at a rate of 1 image every 6 sec following 0.25 sec delay to permit vibrations of the expelled drop to dampen. Drop evaporation rates within the humidified chamber deduced from computed-drop volumes (based on image analysis) were observed to vary with solute concentration, generally ranging from approximately 25 nL/min for pure water to 10 nL/min for solute solutions > 0.1% w/v. Precision of θ_a was about 0.5° based on repeated measurement of the same drop. The analysis chamber was thermostated to a lower-limit of 25±1 °C by means of a computer-controlled resistive heater. Upper-temperature

limit was not controlled but rather floated with laboratory temperature, which occasionally drifted as high as 29 °C during summer months. Thus, reported θ_a values were probably not more accurate than about 1° on an inter-sample basis considering the small, but measurable, variation of water interfacial tension with temperature. Test substrata were held on a rotating, tilting-plate platform driven by stepper motors under computer control. Substrata were allowed to come to equilibrium within the sample-chamber environment for no less than 30 min before contact angle measurements were initiated. The platform was programmed to tilt at 1°/sec from horizontal to 25° after the drop was deposited on the surface by the robot. The first 120 sec (20 images) monitored evolution of the advancing angle.

Captive-drop goniometry (CDG) was implemented using a home-built goniometer, as described elsewhere.⁷ Briefly, CDG involved capturing the droplet on the test surface with a fine needle connected to a 50 μ L syringe. θ_a or θ_r was read by adding or withdrawing water from the drop, respectively. Contact angles were measured from images captured by a CCD camera when observable motion had ceased.

Figure Legend:

Figure 1: Comparison of advancing (θ_a , panel A) and receding (θ_r , panel B) contact angles from goniometric techniques – tilting-plate (TPG, closed circles) and captive-drop (CDG, open circles), to Wilhelmy-balance tensiometry (WBT). Diagonal lines correspond to ideal 1:1 correlation between the techniques. θ_a measured by goniometric methods (TPG and CDG) were in statistical agreement with WBT, whereas θ_r measurements were systematically offset from WBT. Linear regression through advancing angles of TPG and CDG vs. WBT (panel A) yielded [$\theta_a^{TPG} = (0.99 \pm 0.03)\theta_a^{WBT} + (-2.3 \pm 2.9); R^2 = 98\%$] and [$\theta_a^{CDG} = (0.93 \pm 0.06)\theta_a^{WBT} + (2.2 \pm 5.0); R^2 = 94\%$] respectively. Corresponding results for receding angles (panel B) of TPG and CDG vs. WBT yielded [$\theta_r^{TPG} = (1.2 \pm 0.1)\theta_r^{WBT} + (5.3 \pm 6.5); R^2 = 83\%$] and [$\theta_r^{CDG} = (0.9 \pm 0.1)\theta_r^{WBT} + (10.1 \pm 6.7); R^2 = 78\%$] respectively.

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Surface	Method	θ_a WBT	θ_r WBT	θ_a TPG (% diff from θ_a WBT)	θ_r TPG (% diff from θ_r WBT)	θ_a CDG (% diff θ_a WBT)	θ_r CDG (% diff θ_r WBT)
1a	Nyebar* on OTS	120.1	84.1	120.2 (-0.1)	116.5 (38.5)	112.6 (-6.3)	81.4 (-3.1)
2a	OTS	100.0	71.9	99.1 (-0.9)	96.0 (33.5)	96.1 (-3.9)	91.0 (26.6)
2b	OTS	109.1	75.7	102.9 (-5.6)	95.1 (25.6)	105.4 (-3.5)	87.7 (15.9)
2c	OTS	101.8	78.8	102.6 (0.8)	91.5 (16.1)	100.4 (-1.3)	91.5 (16.2)
2d	OTS	101.2	79.8	99.6 (-1.5)	91.1 (14.1)	98.5 (-2.6)	92.2 (15.4)
3a	APTES	76.4	44.3	73.4 (-3.9)	60.9 (37.5)	85.7 (12.2)	63.2 (42.6)
3b	APTES	74.9	34.9	72.7 (-2.9)	63.3 (81.1)	69.7 (-7.1)	44.4 (26.9)
3c	APTES	76.3	44.2	71.6 (-6.1)	70.1 (58.6)	72.1 (-5.6)	61.8 (39.7)
4a	Oxidized OTS ^{††} 5min	77.3	53.5	70.3 (-9.0)	61.4 (14.9)	75.2 (-2.75)	54.1 (1.2)
4b	Oxidized OTS [†] 5min	93.1	56.1	92.6 (-0.5)	82.1 (46.3)	87.4 (-6.2)	80.1 (42.8)
5a	Oxidized OTS [†] 10min	58.5	30.0	56.5 (-3.4)	33.0 (10.1)	58.3 (-0.4)	42.6 (42.2)
5b	Oxidized OTS [†] 10min	82.1	58.5	76.4 (-6.9)	65.4 (11.8)	71.9 (-12.5)	54.6 (-6.6)
6a	Oxidized OTS [†] 15min	51.6	28.2	50.2 (-2.6)	21.2 (-24.6)	48.6 (-5.7)	22.4 (-20.7)
6b	Oxidized OTS [†] 15min	76.1	59.4	72.0 (-5.4)	68.4 (15.0)	66.5 (-12.7)	53.4 (-10.1)
7a	Oxidized OTS [†] 20min	50.2	25.2	51.0 (1.6)	34.0 (36.0)	49.7 (-0.8)	32.2 (27.8)
7b	Oxidized OTS [†] 20min	70.3	44.0	71.1 (1.1)	66.0 (49.9)	79.5 (12.9)	69.0 (56.8)
8a	Oxidized OTS [†] 25min	48.4	23.1	48.0 (-0.8)	31.3 (35.5)	45.6 (-5.8)	35.7 (54.7)
8b	Oxidized OTS [†] 25min	71.8	39.8	62.9 (-12.4)	59.9 (50.4)	64.9 (-9.5)	46.1 (15.6)

Notes: * 1, 1, pentadecafluorooctylmethacrylate deposited on OTS-treated glass.
† Octadecyltrichlorosilane (OTS) treated glass-slide dipped in CrO4/H₂SO₄ solution for specified times.

