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## A Systematic Comparison of Contact Angle Methods

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### Introduction

Among the various modern surface analytical tools available, contact angle and wetting techniques remain as standard methods for benchmarking surface quality.<sup>1</sup> These wetting measurements, which fall within the broader category of tensiometry, are sensitive to the upper 0.5 nm or so of a surface<sup>2,3</sup> and are, therefore, among the most surface-sensitive techniques available. Tensiometry measures the fundamental energetics at an interface that drive adsorption and adhesion.<sup>4</sup> Thus, tensiometric techniques monitor significant interfacial phenomena in diverse technological areas of commercial importance such as adhesion, biomedical materials, electronic materials, and tribology.

As part of our program to use alkylsiloxane self-assembled monolayers (SAMs)<sup>5</sup> as model polymer and biomaterial surfaces, we were interested in careful application of tensiometric characterization techniques.<sup>1,4,6,7</sup> Specifically, we are attracted to Wilhelmy balance tensiometry and contact angle goniometry for measuring contact angle hysteresis because these have become standard methods in the polymer and biomaterial fields. In the goniometer case, the sessile drop and tilting plate methods are in wide application. Although there is a considerable body of literature on the contact angle and wettability (see ref 1 for a recently published text and references cited therein), to our knowledge there is no systematic comparison of these specific techniques that compare accuracy and precision. For example, Seebergh and Berg<sup>8</sup> have compared contact angles determined from Wilhelmy balance force measurements to those obtained through simultaneous optical inspection and found no systematic differences. However, these studies did not compare results of the tilting plate and sessile drop methods of contact goniometry. Ikada and co-workers<sup>9</sup> compared results of contact goniometry and Wilhelmy balance methods, but these studies employed a series of

different polymer films that introduced complications in detailed technique comparison.

We report herein a systematic study of the aforementioned Wilhelmy balance and contact goniometer methods using SAMs as high-quality, homogeneous surface analytical standards. Since the SAM surface is arguably more "perfect" than previously available organic thin films, information obtained from tensiometric measurements on SAMs can be more clearly interpreted in terms of subtle technique-to-technique differences. Moreover, since SAMs can be reproducibly prepared,<sup>5,6</sup> a statistically significant set of observations can be made to measure inter and intratechnique precision. It is our hope that these results will be useful to other researchers contemplating use of the Wilhelmy balance and contact angle goniometry.

### Results and Discussion

The important question probed herein asks if the Wilhelmy balance and goniometer methods (tilting plate and sessile drop techniques) yield identical measures of contact angle hysteresis (the difference between advancing and receding contact angles<sup>11-14</sup>). Differences between methods might arise because, in the balance method, the solid-liquid-vapor (SLV) three-phase line is in wholesale motion whereas the SLV line is essentially static in the goniometric approaches. Also, there are significant instrumental differences. For example, contact angles are calculated from force measurements in the Wilhelmy balance case, as will be discussed in more detail presently, rather than directly observed as in the goniometer case. In the tilting plate, the droplet is tilted "to the point of incipient motion" in order to obtain the maximum advancing angles and the drop is free to move. This is in contrast to the sessile drop method in which the droplet is captured by a thin syringe needle through which the liquid is added or withdrawn for the reading of the advancing and receding angles, respectively.

We have attempted to hold all other variables constant to minimize extraneous sources of systematic error that might influence the comparison of techniques. For example, we practiced contact angle goniometer methods in such a way as to minimize or eliminate droplet motion by use of a vibration-isolation table and slow, motorized tilt-stage apparatus. Solutions employed herein were pure water containing no surfactants so that solute adsorption effects could be eliminated as a causative agent of differences between techniques.<sup>7,10</sup> SAM surfaces were well-defined and reproducibly prepared so that macroscopic variations in surface quality were minimized and microscopic heterogeneity was substantially identical from specimen to specimen or spot to spot on a given test substratum. Finally, more than 400 contact angle measurements were made on more than 20 individually prepared SAM surfaces on both polished silicon and glass

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**Table I. Comparison of Contact Angle ( $\theta$ ) Values<sup>a</sup> from Different Tensiometric Methods: HTS Monolayers on Silicon**

	Wilhelmy balance	tilting stage	syringe
$\theta_a$ (deg)	112.7 $\pm$ 0.8	110.3 $\pm$ 1.9	106.0 $\pm$ 2.4
$\theta_r$ (deg)	96.0 $\pm$ 1.0	90.3 $\pm$ 2.2	94.9 $\pm$ 2.5
$\theta_a - \theta_r$	16.7 $\pm$ 1.3	20.0 $\pm$ 2.9	11.1 $\pm$ 3.5
no. of Plates	10	8	8
<i>n</i>	30	60	80

<sup>a</sup> Contact angles are mean values  $\pm$  standard deviations based on *n* measurements.

**Table II. Comparison of Contact Angle ( $\theta$ ) Values<sup>a</sup> from Different Tensiometric Methods: HTS Monolayers on Glass Coverslips**

	Wilhelmy <sup>b</sup> balance	tilting stage	syringe
$\theta_a$ (deg)	103.7 $\pm$ 4.9	108.2 $\pm$ 1.5	102.6 $\pm$ 1.8
$\theta_r$ (deg)	87.0 $\pm$ 5.0	88.8 $\pm$ 2.0	94.4 $\pm$ 2.0
$\theta_a - \theta_r$	20.5 $\pm$ 6.3	19.4 $\pm$ 2.5	8.2 $\pm$ 2.7
no. of Plates	10	8	8
<i>n</i>	50	60	80

<sup>a</sup> Contact angles are mean values  $\pm$  standard deviations based on *n* measurements. <sup>b</sup> The advancing angle is immersion cycle dependent;  $\theta_a = 107.6^\circ \pm 3.8^\circ$  for the first immersion. For subsequent immersions,  $\theta_a$  decreases to  $103.7^\circ \pm 4.9^\circ$  and remains constant thereafter. The receding angle does not change (see text for further discussion).

coverslips, yielding a statistically significant basis for our conclusions.

The fundamental energetic measured in tensiometry is adhesion tension,  $\tau = \gamma_{(lv)} \cos \theta$ , where  $\gamma_{(lv)}$  is the liquid-vapor (lv) interfacial tension and  $\theta$  is the contact angle. Adhesion tension is directly measured in the balance case whereas  $\theta$  values are observed in contact angle goniometry. Direct comparison of Wilhelmy balance and goniometer results involves conversion of adhesion tension to  $\theta$  by use of separate  $\gamma_{(lv)}$  measurements. Alternatively, a "synthetic"  $\tau$  can be calculated from  $\theta$  observations.

We used glass coverslips and semiconductor-grade silicon as substrata for our studies, representing surfaces which might be prepared on ordinary glass labware and those on an idealized polished substratum, respectively. The plates were coated in a drybox using freshly distilled hexadecyltrichlorosilane (HTS) in purified hexadecane. The water contact angles of the HTS SAMs were then determined using the three different tensiometric methods. The Wilhelmy balance method has been described previously.<sup>7</sup> The tilting plate method involves observation of the contact angle formed by a droplet of liquid on the surface of interest as it is tilted from the horizontal. The advancing angle is read from the leading droplet edge whereas the receding angle is read from the trailing droplet edge. The droplet is not moving while the measurement is taking place, but is rather at the point of incipient rolling. The sessile drop method involves expanding or contracting a contact angle droplet on a surface by the addition or withdrawal of fluid using a microsyringe setup. As in the tilting plate method, the advancing angle is read from the leading droplet edge (filling mode) whereas the receding angle is read from the trailing droplet edge (emptying mode).

Contact angle measurements using the three methods for HTS monolayers on silicon and glass are listed in Tables I and II, respectively. Generally speaking, the Wilhelmy balance gave the highest values for advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) angles. Hysteresis curves were more stable and repeatable over four separate immersion cycles

observed for each silicon specimen.<sup>15</sup> On glass, however, the first immersion cycle ( $\theta_a \approx 108^\circ$ ) was always markedly different from that of subsequent immersions. The stable final angle is reported in Table II. Results of the tilting plate method are very close, but not statistically equivalent, to those of the Wilhelmy balance. By contrast, results from the sessile drop method were in substantial variance with either the balance or plate method. In addition, the sessile values were lower than those obtained by either Wasserman and co-workers<sup>16</sup> ( $\theta_a = 110^\circ$ ) or Moaz and Sagiv<sup>17</sup> ( $\theta_a = 112^\circ$ ) for similar SAMs prepared on silicon. The sessile drop method gave the lowest hysteresis ( $\theta_a - \theta_r$ ) because the advancing angles were the lowest and receding angles highest among the methods. The presence of the needle in the droplet creates a second three-phase boundary which is a possible explanation for the difference. Operator skill is also a consideration although we have tried to minimize this by multiple operators and large data sets.

## Conclusions

No single contact angle characterizes a surface. Instead, a maximal advancing angle and minimal receding angle are observed, with a range of metastable angles observed in between these boundaries. An important question that arises in the detailed analysis of contact angle hysteresis on different surfaces asks which tensiometric method yields the most accurate and precise advancing and receding angles. This work compared three popular tensiometric methods using a statistically significant set of carefully prepared, self-assembled silane monolayers on silicon and glass substrata. Results of this study corroborate previous work<sup>7</sup> indicating that the Wilhelmy balance and the tilting plate method yield very similar measures of contact angle hysteresis and the highest advancing angles. The sessile drop method gave significantly different measures of advancing and receding angles. In our hands, the sessile drop method was the most difficult to reproducibly perform.

We conclude that the Wilhelmy balance is the best technique for measuring contact hysteresis. This is based not only on the fact that the highest advancing angles are obtained but also on the facts that (1) the balance technique reduces or eliminates operator subjectivity, particularly when advanced computational techniques are applied,<sup>15</sup> and (2) a much larger surface area is sampled than in the goniometer methods. When the balance method is not possible to perform, the tilting plate method is recommended. The sessile drop method is not recommended by this study because of operator subjectivity and difficulty in performing the method. Results obtained are significantly different from those of the tilting plate or Wilhelmy balance method.

## Experimental Section

Hexadecyltrichlorosilane (HTS, purchased from Hüls) was vacuum distilled (bp 150–155 °C at 0.4 mmHg) prior to use. Hexadecane (Aldrich) was purified by percolation twice through neutral alumina (Aldrich, used as received) and stored over molecular sieves (4 Å, Fisher Scientific). The silicon wafers (Semiconductor Processing Co., Boston, MA; two-side polished, type N) and glass slides (Fisher Scientific, 22  $\times$  50  $\times$  0.1 mm; Clay Adams "Gold Seal No. 1") were cleaned using "piranha" solution.<sup>13</sup> Cleaned substrates were immediately immersed in a 0.3% solution of HTS in hexadecane inside an argon-purged

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drybox. Ten glass and ten silicon samples were prepared in a single batch and were stored in fluoroware containers until analysis. Physiological saline solution (Abbott Laboratories) was used as the test liquid for all contact angle measurements ( $\gamma_{lv}$ ) = 72.6 dyn/cm).

Wilhelmy balance measurements of contact angles were carried out using a Cahn SFA-212 (Cahn Instruments, Inc.) equipped with the appropriate software. Tilting stage and syringe method measurements were done with a Rame-Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base. The syringe method for determination of advancing and receding contact angles followed the technique used by Johnson and Dettre.<sup>11</sup>

Statistically invalid measurements were identified by a stan-

dard method for determining outliers.<sup>18</sup> Analysis of variance was then used to compare the three techniques simultaneously (both advancing and receding angle data were compared separately). Also  $Z$  values were calculated to compare two techniques at a time.

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