

Contact Angle Goniometry as a Tool for Surface Tension Measurements of Solids, Using Zisman Plot Method

A Physical Chemistry Experiment

Konrad Kabza,^{†*} Jason E. Gestwicki, and Jessica L. McGrath

Department of Chemistry, SUNY at Fredonia, Fredonia, NY 14063; *kkabza@selu.edu

Surface science, in particular its experimental aspects, is not in the forefront of today's undergraduate physical chemistry curricula. One reason is usually a very packed sequence of experimental physical chemistry. This puts a fundamental question before a lecturer: which experiments to eliminate in order to accommodate the new ones. Our philosophy is not necessarily to eliminate but rather to modify the existing experiments, so as to accommodate new-sprung and interesting fields such as surface science.

Most textbooks for experimental physical chemistry include rudimentary experiments from the field of surface science—for example, such classics as measurement of surface tension of liquids, or wetting. These can easily be expanded by incorporation of our experiment. The relevance of the surface tension of solids to physical chemistry is unquestionable. Surface tension pertains to concepts of surface free energy, adhesion, and wetting. It also demonstrates some fundamental properties and phenomena such as intermolecular interactions (ion–dipole, dipole–dipole, and Van der Waals forces). Some of these properties can actually be visualized through the behavior of a drop of liquid on the surface of an analyte.

In recent years very few experiments dedicated to the measurement of surface properties have been reported. It is understood that the equipment required to perform such measurements is usually very specialized and often expensive. Nonetheless, there are sources of accurate yet inexpensive instruments perfectly suited to enhance the undergraduate experience in physical chemistry laboratory. These include commercial tensiometers, Wilhelmy balances, and contact angle goniometers as well as “homemade” instruments, which are much cheaper (1). Thus, expense should not preclude the introduction of surface phenomena experiments in physical chemistry laboratory sequences.

Background

Contact angle measurements date to the early days of the 19th century, when Laplace and Young tried to formalize wetting behavior using the methods of then-new differential calculus. These measurements allow insight into the most fundamental properties of both liquids and solids, including their cohesive forces, adhesive behavior, wetting properties, and morphological properties. However, although contact angle theory has been introduced in physical chemistry for decades (2), laboratory manuals and their experiments seldom utilize the concept. Nevertheless, the interdisciplinary nature of the topic has placed it in some unexpected texts, as for example Clark Most's *Experimental Organic Chemistry*.

[†]Present address: Department of Chemistry and Physics, South-eastern Louisiana University, Hammond, LA 70402.

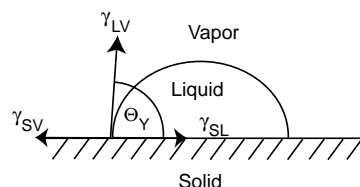


Figure 1. Graphical vector representation of sessile drop parameters: Θ_Y , Young's contact angle; γ_{SV} , solid–vapor interfacial free energy; γ_{LV} , liquid–vapor interfacial free energy; γ_{SL} , solid–liquid interfacial free energy.

Students are usually fascinated by the concepts that relate to contact angle goniometry. Very often it is the first time they see relationships between the wetting of materials and the macroscopic shape of the drop. Such observations permit logical conclusions about why Teflon is a good coating for a frying pan, and visualization of the drop's behavior helps students to understand the molecular properties of the material. Van der Waals interactions gain real meaning, as do polar–nonpolar interactions. Students very quickly learn to make predictions about materials' adhesive and polar properties based on their measurements of contact angles. In addition, the ability to quantify the observed relationships by measuring contact angles allows students to build a library of materials' properties and to see trends. This is illustrated by analyzing a series of polymers such as poly(vinyl chloride), each chlorinated to a different degree. The more chlorinated the sample is, the lower is the contact angle as measured with water.

Contact angle measurements are very surface-specific. The technique reportedly analyzes the outermost 5 Å of a material (3). By observing the contact angle formed by a liquid in contact with a solid surface, information about the surface tension and surface energy of the material can be obtained. Figure 1 illustrates a sessile drop of probing liquid in contact with the analyzed surface (4). The surface free energies (γ_{SV} , γ_{LV} , γ_{SL}) and the Young's contact angle (Θ_Y) are interrelated as shown in eq 1.

$$\cos \Theta_Y = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV} \quad (1)$$

Although many researchers consider contact angle goniometry a purely qualitative technique (5), it can be employed to measure certain properties in a quantitative way (6). Particularly useful are measurements in which advancing or receding contact angles are used. These angles are much more accurate and take into account such experimental irregularities as surface roughness, morphology, and inhomogeneity. However, measurement of advancing or receding contact angles is difficult and much more time consuming than measurement

Table 1. Surface Tension of Organic Compounds in Water

Solute	Wt % of Solute and Surface Tension, γ / mN m ⁻¹ ^a							
Acetonitrile	1.13	3.35	11.77	20.20	37.58	61.33	81.22	— ^b
	<i>69.02</i>	<i>63.03</i>	<i>47.61</i>	<i>39.06</i>	<i>31.84</i>	<i>30.02</i>	<i>29.02</i>	
<i>n</i> -Propanol	0.1	0.5	1.0	— ^b				
	<i>67.10</i>	<i>56.18</i>	<i>49.30</i>					
Dioxan	0.44	2.20	4.70	11.14	20.17	35.20	55.00	67.68
	<i>69.83</i>	<i>65.64</i>	<i>62.45</i>	<i>56.90</i>	<i>51.57</i>	<i>45.30</i>	<i>39.27</i>	<i>36.95</i>
Acetic acid	1	2.475	5.001	10.01	30.09	49.96	— ^b	
	<i>68.0</i>	<i>64.4</i>	<i>60.1</i>	<i>54.6</i>	<i>43.6</i>	<i>38.4</i>		

^aValues for γ are in italic type. They were obtained from ref 9.

^bMore concentrated solutions had impractically low surface tension and contact angles could not be measured.

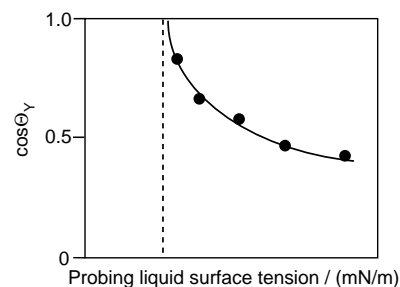


Figure 2. A typical Zisman plot.

of simple Young's angles. This is particularly true for a casual contact angle goniometer user. Thus, we have based our entire experiment on measurement of Young's angles.

Measurement of Young's Contact Angle

The technique of measuring Young's contact angles was described previously (7) in detail, but its main facets will be presented for the benefit of novices to the method. To find Young's contact angle for a liquid in contact with a surface, a drop of the liquid is placed on a horizontal surface. Both the drop and the material on which it is placed have to be enclosed inside an environmental chamber (100% humidity), a small container partially filled with the liquid of interest and equipped with optically clear windows. The drop (typically 1 μ L) is placed on the surface of the material and oriented in such a way that the instrument's crosshair is tangent to the cross-sectional curvature of the drop at a point where all three media (solid, liquid, and vapor) meet (see Fig. 1). The angle between the crosshair and the base of the drop is read off the protractor and recorded as Young's contact angle. Two general conditions must be fulfilled in the process of contact angle goniometry: the analyzed surface cannot be reactive towards the analyzing liquid, and the drop must be stable (not changing shape) while in contact with the surface.

The Zisman Plot

Zisman's method for obtaining the material's surface tension is based on the experimental finding that when a liquid spreads freely on an analyzed surface, its surface tension is lower than or equal to that of the surface upon which it is spreading. Zisman called the value of the surface tension of the liquid that is equal to that of the analyzed material γ_c (critical surface tension). To obtain the γ_c value, a series of contact angles is measured using liquids with progressively smaller surface tensions. The surface tension of these liquids is then plotted against the cosine value of the corresponding contact angle (Fig. 2). The solid line in Figure 2 represents a best fit for the measured points and is extrapolated to intersect with the value of $\cos \Theta_Y = 1$. At the point of the intersection a line (dashed line) is drawn perpendicular to the x axis and a value of γ_c can be obtained. This protocol for obtaining γ_c is typically repeated for a variety of liquids; and qualitatively, at least, the critical surface tensions for homologous liquids, on the same surface, correlate.

Experimental Procedure

Contact angles were measured using a contact angle goniometer constructed in-house (1). Sixteen measurements, each performed on a virgin site of the analyzed material, were recorded and averaged for each surface-liquid combination. All values represented Young's contact angle. Both the drop and the material on which it was placed were inside an environmental chamber at 100% humidity with respect to the liquid of interest. Measurements were made at ambient temperature, using probing solutions of four organic liquids (acetonitrile, propanol, dioxane, and acetic acid) diluted with a Millipore-deionized water. Table 1 shows the concentrations of the probing liquids utilized.

The process of obtaining a set of dilution standards of known surface tension, like the one presented in Table 1, can be a supplementary experiment. Students could prepare a set of solutions and measure their surface tension using the capillary rise method and subsequently use these solutions to obtain contact angles on a variety of surfaces. An existing experiment can easily be adapted to serve this purpose (8).

All drops were of equal size (1- μ L). Measurements were taken after a 5-30-s equilibration in the environmental chamber. Samples were mounted on 1 \times 2-cm glass slides with the help of double-sided Scotch 3-M tape. The standard deviation calculated from 14-16 measurements on each surface never exceeded $\pm 4^\circ$. Typically, commercial goniometers have an accuracy of $\pm 2^\circ$ for a single user and $\pm 3^\circ$ for multiple users. Four types of materials were analyzed: Teflon tape, glass slides, polyethylene film (brand-new trash bag), and acetate transparencies. Except for acetate transparencies, which were wiped clean with a Kimwipe wetted in absolute ethanol, surfaces were not treated prior to the measurements. All data analysis and graphical interpretation were performed using Delta Graph Pro 3.0 from Delta Point, Inc., on a Macintosh computer.

Results and Discussion

The measurements obtained in our experiment are comparable to those previously published (Table 2) even though we depended on Young's values rather than advancing contact angles. The judicious choice of materials for analysis made it easier to see the differences of wetting of those materials with the same probing liquids. Availability of these materials was an important factor as well. We tried to utilize common materials that any undergraduate laboratory would have access to.

Table 2. Comparison of Values for Surface Tension of Some Solids

Material	$\gamma_c / \text{mN m}^{-1}$		
	Measured	Literature (5c)	Typical Estimate (5c)
Polyethylene film	24–30	25–33	33
Teflon tape	6–12	6–25	18
Glass slide	28–32	varying	varying
Acetate transparency	28–34	not available	not available

Our data are presented in Figure 3, which represents data sets for four surfaces. For example, Figure 3A represents Young's contact angle measurements on glass slides. Four liquids were used to obtain four values of γ_c : acetonitrile, propanol, dioxane, and acetic acid. The choice of probing liquids was dictated not only by their wetting behavior but also by their relatively low toxicity. As can be seen in Figure 3A, all lines representing best-fit regressions (R^2 value $\geq .95$ for each liquid) intersect the $\cos \Theta_Y = 1$ line at approximately the same point. In fact, they give a very good (narrow) range for the $\gamma_c \approx 30 \text{ mN m}^{-1}$. All the probing liquids produced relatively straight best-fit curves with the exception of the acetonitrile–water combination. This was unexpected, and in fact, for the surface of Teflon, the acetonitrile–water system failed to correlate with other liquids.

Conclusion

This experiment is a simple and dependable method for obtaining surface tensions of a variety of solids. It provides an introduction to the fascinating field of surface science at a suitable level for undergraduate physical chemistry. We also believe it has value in data interpretation and statistical analysis, which are so important in all areas of modern science. Owing to limited access to the instrumentation, group work was found to facilitate incorporation of this experiment into the physical chemistry laboratory sequence.

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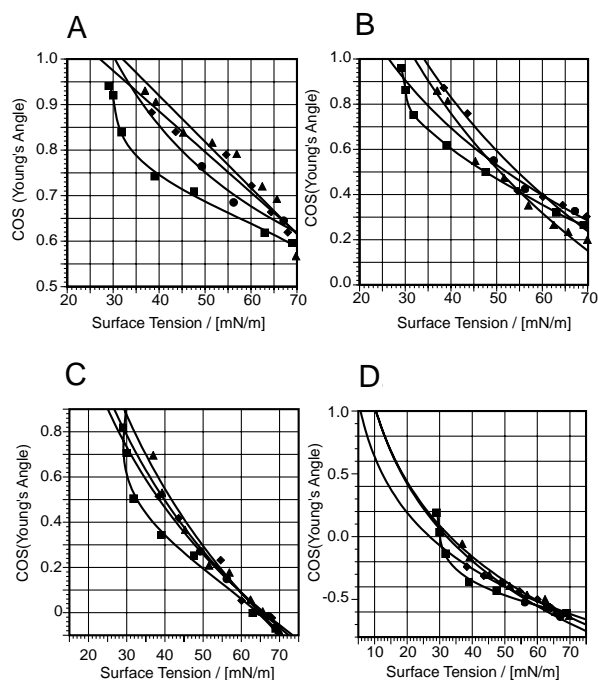


Figure 3. Wettability of surfaces. In each graph four liquids were used, *n*-propanol (●), acetic acid (◆), dioxane (▲), acetonitrile (■). A: Glass surface. B: Acetate surface. C: Polyethylene surface. D: Teflon surface.

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