Brighton Science

Evaluating the Influence of Temperature and Humidity on Surface Energy and Contact Angle

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Customers often ask how deviations from "standard" ambient conditions (typically 22°C (72°F) and 30% relative humidity affect water contact angle measurements. These concerns may also extend to measurements taken on surfaces that are hotter or colder than the surrounding environment. To address this, it's important to first understand what determines a contact angle and then examine how variations in temperature and humidity may influence measurement.

The contact angle formed between a liquid with a surface is determined by three factors: the surface tension of the liquid, the surface energy of the solid, and the way the liquid is deposited onto the surface. The relationship between liquid surface tension γ_{lv}, solid surface energy γ_{sv}, interfacial energy γ_{sll}, and contact angle θ is expressed by the Young equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$$

This relationship shows that the measured contact angle is governed by the balance of surface and interfacial energies. Accordingly, any effects of temperature or humidity on contact angle measurements must result from changes in these energies.
With this framework in mind, the effects of temperature and humidity on water contact angle can be considered in terms of how they influence surface and interfacial energies.

Temperature Effects:

Surface energy is equivalent to the chemical reactivity of a surface (determined by the number of active sites per unit area and the reactivity of those sites). Temperature influences surface energy through its effect on molecular motion and surface structure. As temperature increases, the amplitude of molecular vibrations increases, causing thermal expansion of the surface. This expansion increases the distance between active sites, reducing the number of active sites per unit area, and consequently decreasing surface energy.
A similar temperature dependence applies to the probe liquid. The surface tension of water (γ_{lv}) decreases with increasing temperature and can be estimated using Eötvös rule, which describes the relationship between temperature and liquid surface tension:

$$\gamma = 0.07275\frac{N}{m} * \left(1 - 0.002 * (T - 291\ K)\right)$$

Empirical studies have likewise shown that polymer surface energies decrease with temperature, with a relatively small temperature coefficient (0.06°C^{-1}) over typical operating conditions. Because contact angle is determined by the balance between liquid surface tension (γ_{lv}) and solid surface energy (γ_{sv}), these concurrent decreases tend to offset one another. As a result, the net effect on the measured contact angle is minimal across a wide range of temperatures.

Figure 1 illustrates this relationship, showing the temperature dependence of water surface energy (γ_{lv}), polyolefin polymer surface energy (γ_{sv}), and the resulting contact angle (θ).The slight decrease in both (γ_{lv}) and (γ_{sv}) tend to cancel each other out, resulting in no significant change in contact angle.

Note: This treatment assumes that the interfacial energy (γ_{sl}) remains constant over this temperature range. This term represents the residual energy at the interface after interaction between the liquid and the solid and is not expected to change significantly under these temperatures.

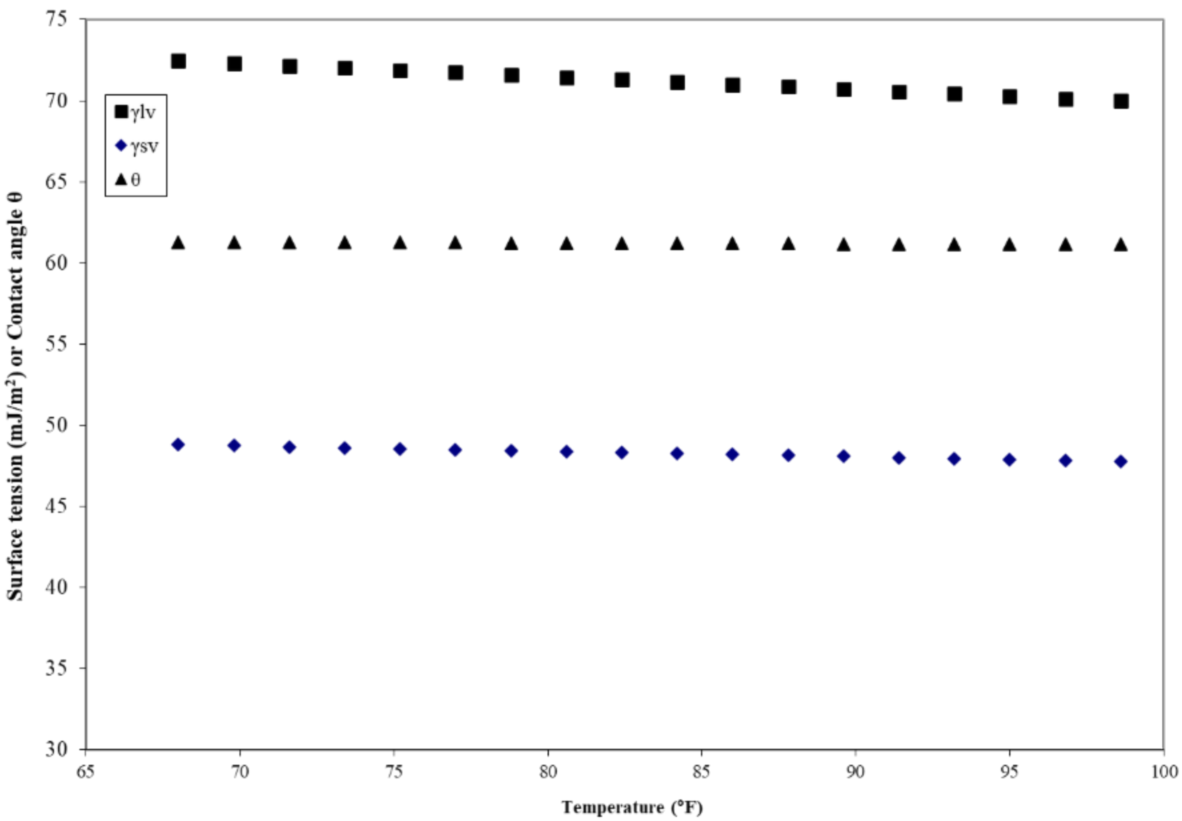

Figure 1. Effect of temperature on surface tension of water, surface energy of a polymer, and the resulting contact angle.

Viscosity Effects:

Temperature affects the viscosity of the probe liquid, which can influence the dynamics of how a droplet forms and spreads when deposited onto a surface for analysis. This, in turn, can affect the measured contact angle through contact angle hysteresis.

Hysteresis is the difference between the two extremes of contact angle that can be established with a surface, known as the advancing angle (established as a liquid slowly wets a surface) and the receding angle (established as a liquid retracts from a previously wetted surface). Most contact angle measurements represent the advancing angle, typically made by gently depositing the liquid onto the surface.

Because viscosity decreases significantly with increasing temperature, one might expect changes in droplet formation dynamics to influence the measured contact angle. While this can be a problem with standard contact angle goniometers, temperature compensation built into the Surface Analyst deposition system minimizes these effects. In the case of the Surface Analyst, drop formation is governed by a precisely controlled, repeatable deposition (Ballistic Drop Deposition), which compensates for viscosity-related changes.
Figure 2 shows the change in viscosity of water with temperature.

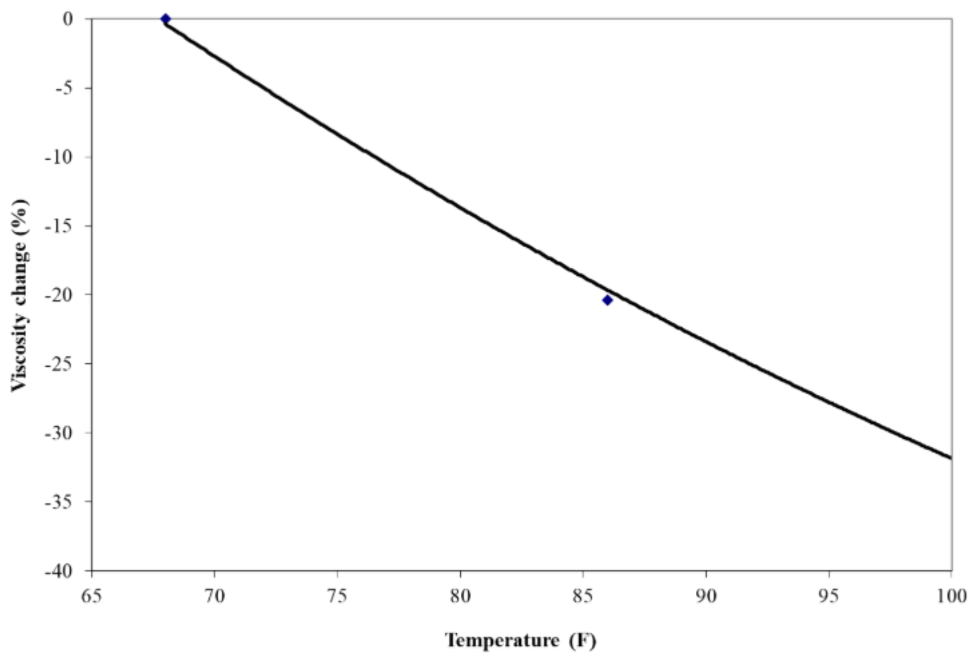

Figure 2. Effect of temperature on water viscosity.

Humidity Effects:

Relative humidity does not directly influence water contact angle measurements, as these measurements are performed using a liquid that is already in equilibrium with its vapor phase. As a result, changes in ambient humidity do not significantly affect the surface tension of the probe liquid during measurement.

Humidity can indirectly influence contact angle by altering the surface energy of the solid over time. Exposure to elevated humidity may promote surface reactions such as corrosion, which can modify the chemical composition and reactivity of the surface. These changes, if present, would be reflected in the measured contact angle.

To evaluate the combined effects of temperature and humidity, instruments were stored under controlled environmental conditions ranging from 50°F / 15% RH to 80°F / 90% RH for up to 96 hours. Water contact angle measurements taken over this period remained consistent and within the measurement standard deviation for these surfaces.

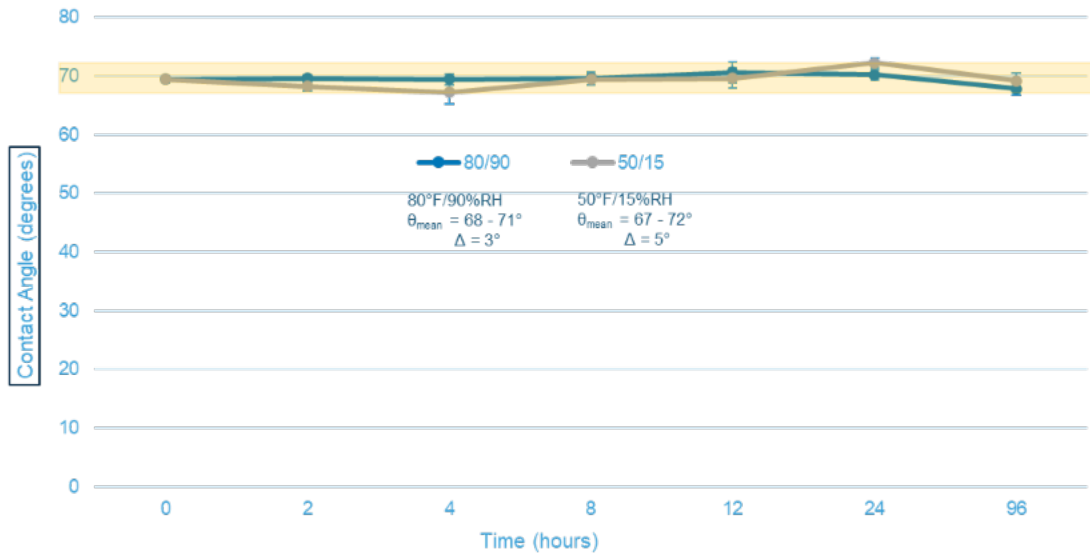

Figure 3. Effect of temperature and humidity on water contact angles measured on a test surface using the Surface Analyst. Instruments were stored in environmental chambers at either 80°F/90%RH or 50°F/15% RH for up to 96 hours with contact angle measurements taken at various intervals.

Conclusions:

Contact angle measurements are governed by the balance between liquid surface tension and solid surface energy. While both temperature and humidity can influence these underlying properties, their effects are either minimal or indirect under typical measurement conditions. Temperature produces small, parallel decreases in both liquid surface tension and solid surface energy. Because contact angle depends on the balance between these terms, these changes largely offset one another. Although temperature also affects liquid viscosity, controlled deposition methods minimize its influence on droplet formation and contact angle hysteresis.

Relative humidity does not directly affect contact angle measurements, as the measurement is defined by the interaction between a liquid in equilibrium with its vapor phase and the surface. However, prolonged exposure to humid environments can alter surface chemistry over time, which may influence measured values. These changes reflect true modifications to the surface rather than variability in the measurement itself.

Contact angle measurements are robust to typical variations in environmental conditions. As a result, deviations from standard temperature and humidity conditions do not represent a significant source of measurement error, and measurements can be confidently performed across a broad range of real-world conditions.

References

1. Polymer Surfaces, B.W. Cherry (Cambridge Univ. Press, 1981).