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Todd P. Silverstein

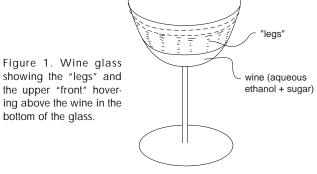
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Many people who consume noncarbonated alcoholic beverages notice that "legs" seem to run continually up and down the inside surface of the glass. This can be seen particularly well in clean, clear glasses with regular, rounded inner surfaces. After drinkers take a sip of wine, brandy, or port, they may notice thin streams of liquid descending toward the bottom of the glass, and then back up toward the top again (see Fig. 1). These legs may persist for several minutes after each sip. The phenomenon is a curious one: how can a stream of liquid spontaneously rise toward the top of a glass?

Consider these related phenomena: (i) capillary action causes aqueous solutions to rise through narrow tubes to a point significantly above the solution level; and (ii) the meniscus of a column of water curves upward because water close to the tube's inner surface rises above the solution level. All three of these phenomena—the concave meniscus, capillary action, and legs in a wine glass—stem from intermolecular forces. The peculiarities of how water molecules attract each other (*cohesive* forces) vs how water molecules are attracted to solid polar surfaces (*adhesive* forces) figure prominently in explaining these curious phenomena.

Polar molecules attract each other with relatively strong dipole-dipole intermolecular forces. A common type of dipole–dipole interaction is the *hydrogen bond*, which stems from the attraction between a partially positive hydrogen atom and a lone pair of electrons on a nearby small, highly electronegative atom such as oxygen, nitrogen, or fluorine. Water, H–O–H, has two hydrogens and two oxygen lone pairs per molecule; thus each water molecule has four possible hydrogen-bonding sites (see Fig. 2). Extensive hydrogen bonding between water molecules makes for strong cohesive forces, which in turn account for the relatively high viscosity and surface tension of liquid water. Ethanol, in contrast, is less viscous than water: CH₃CH₂OH has only a single polar O-H group, allowing just three possible hydrogen-bonding sites per molecule (see Fig. 2). Finally, consider the fact that glycerol is much more viscous than water. The tri-alcohol $C_3H_5(OH)_3$ has three O–H groups, allowing nine possible hydrogen-bonding sites in each molecule.

What happens when a polar liquid comes in contact with the surface of a polar solid? Cohesive forces still tend to hold the liquid together, giving it a strong, measurable *surface tension*. On the other hand, dipole–dipole forces will also tend to attract the liquid molecules to the solid surface. These *adhesive forces* will tend to make the liquid spread out across the surface of the solid (1). How much a drop of liquid spreads across a solid surface is determined by the relative strengths of the adhesive and cohesive forces. As discussed above, cohesive forces are strongest for glycerol and weakest for ethanol, with water in the middle. Interestingly enough though, adhesive forces between these three liquids and polar surfaces such as glass are rather similar. Accordingly, when placed on a glass surface, drops of ethanol tend to spread the



most: adhesive forces outweigh the weak cohesive forces. Water and glycerol, however, tend to form tight drops with strong surface tension: strong cohesive forces outweigh the adhesive forces.

The same argument explains the physical foundation of capillary action and water's concave meniscus. Close to the inner surface of a glass tube holding a column of water, interaction with the surface is strong; furthermore, the number of surrounding water molecules is less than in the bulk liquid. Accordingly, adhesive forces outweigh cohesive forces and water rises up the inner surface of the glass, forming a concave meniscus. If the tube is narrow enough and adhesive forces are strong enough, the entire aqueous column may rise, producing the phenomenon of capillary action. Because water rising through narrower columns experiences both stronger adhesive forces and weaker cohesive forces, the narrower the tube, the more pronounced its capillary action. In trees, the combination of extremely narrow polar transport tubes (xylem) and efficient evaporation through leaf stomata enables sap to rise all the way from the roots to the treetop via simple capillary action.

Now we are ready to explain our initial conundrum: why do "legs" rise in a wine glass? After you take a sip of wine and then put the glass down, under the influence of gravity, wine from the rim of the glass falls to the liquid surface. Keep in mind however that ethanol has cohesive forces that are substantially weaker than those found in water; at the same time, its adhesive forces toward the polar glass surface are

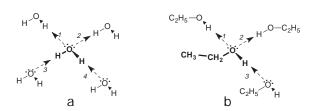


Figure 2. (a) Water, showing four possible H-bonding sites per H₂O molecule. (b) Ethanol, showing three possible H-bonding sites per CH₃CH₂OH molecule.

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roughly equivalent to those found in water. Accordingly, some of the wine may remain suspended above the level of the liquid, because the adhesive forces attracting it to the glass surface are stronger than both gravity and the cohesive forces attracting it to the pool of wine in the bottom of the glass.

Wine close to the rim thus "hovers" over the rest of the wine in the glass, spread in a thin front around the inside of the glass. However, ethanol quickly evaporates from the hovering wine front. As ethanol concentration decreases, cohesive forces increase, and the wine eventually falls in a thin stream down toward the surface of the wine in the bottom of the glass. Upon hitting the surface, ethanol concentration in the falling stream is replenished, cohesive forces decrease, and the stream actually rises up the inside of the glass, back toward the hovering front. The thin streams of rising and

falling liquid constitute the legs of the wine. The process continues unabated for many minutes after each sip.

Most introductory chemistry courses include a discussion of the properties of condensed phases, including the intermolecular forces that dominate in liquids and solids. Illustrating these concepts with well-known everyday examples such as viscosity, surface tension, and capillary action helps students to both visualize and comprehend the ideas of intermolecular cohesive and adhesive forces. A simple, elegant inclass demonstration and discussion of the legs in a wine glass gives students a window on the chemical forces underlying our day-to-day existence.

Literature Cited

1. Silverstein, Todd P. J. Chem. Educ. 1993, 70, 253.