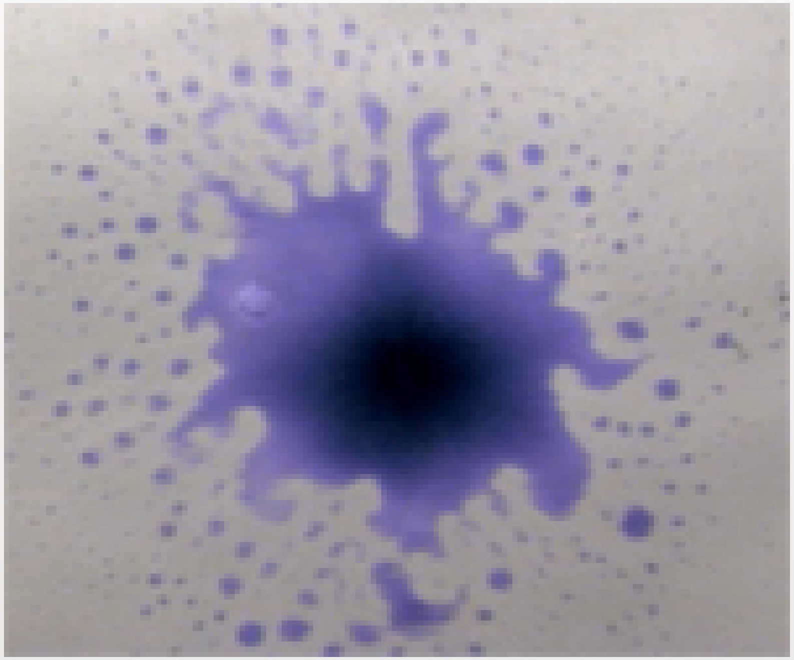
# Interfacial Instabilities in Liquid-Liquid Systems of n-alcohols and Water



3-octanol on 55.6°C $H_2O$

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# Introduction

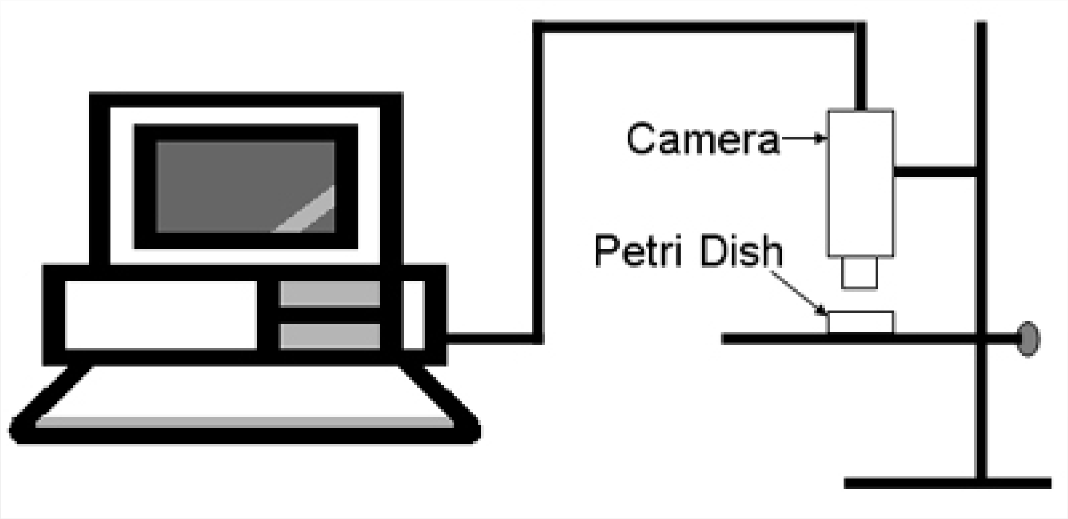
The behavior of a liquid drop on a solid or liquid surface can vary greatly depending on the properties of the materials in contact. Such spreading behavior of a liquid on a material is relevant to many important processes and studies including mixing, coating, spraying, microfluidic devices and biology. Surfactants inside the lungs are critical in preventing lung surfaces from sticking together and collapsing.

For a liquid drop on a liquid surface, under some conditions surface tension gradients can create large-scale flows in the liquid by the Marangoni effect. This and related topics have been researched for years. Thomson observed several of these effects as early as 1855. These usually involved the classic “tears of wine” example.

To date, studies of the Marangoni effect have primarily focused on miscible liquids such as the study of aqueous surfactant drops on thin layers of short-chain alcohols (Chowdhury, 2004). All that was found on n-alcohol drops dealing with surface tension was a study of surface tension oscillations observed in a droplet of n-octanol suspended under water (Kovalchuk, 2000).

In the present study, we have examined the Marangoni effect at the interface between slightly soluble but immiscible fluids, namely water and long chain alcohols (n = 5-10), which we could not find any documentation on. Behavior in these systems was found to display a surprising degree of complexity.

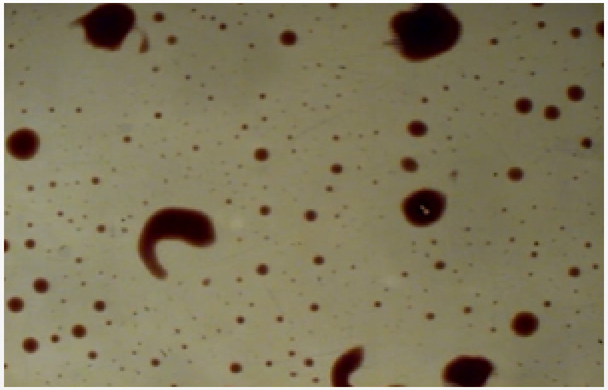
# Experimental Setup

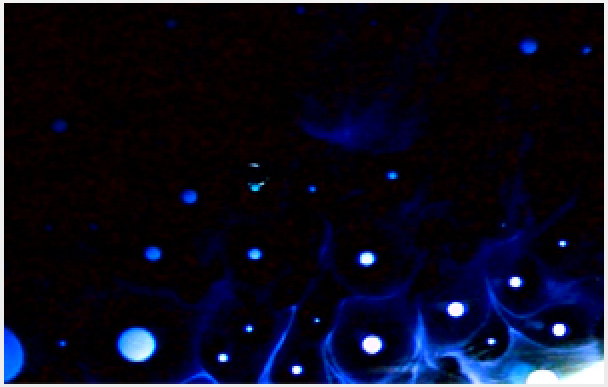



Distilled water was used throughout the experiments. The standard dish that held the water had a diameter of 5.3cm. Other dishes used had diameters of 2.5cm and 6.8cm. A video camera was used to film the experiments. The droplets were hand-dropped or touched to the water surface in volumes ranging from 5-25uL. The videos were recorded at 30 frames per second with a resolution of 720 x 480 pixels. Frame-by-frame analysis of the droplets was done using Scion Image.

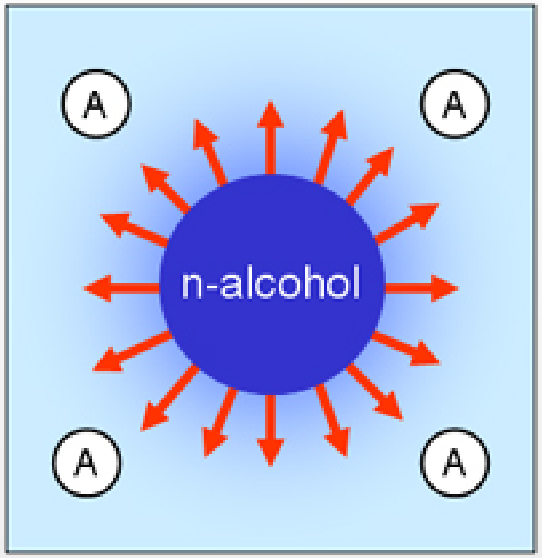
# The Divorce

As the drops move closer together, the alcohol concentration between the drops becomes higher than the concentration surrounding the pair. The higher surface tension surrounding the pair then draws the drops back apart. The alcohol content between the drops is well illustrated in the lower right hand figure. In this picture the drops were dyed with Rhodamin-6G and illuminated with a Hg lamp. Once the drops separate, they don’t ever touch again. The divorce is final.

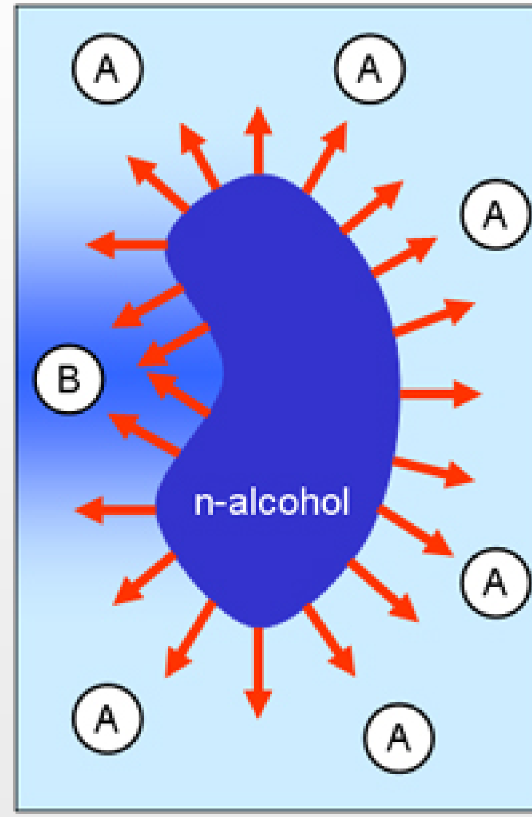




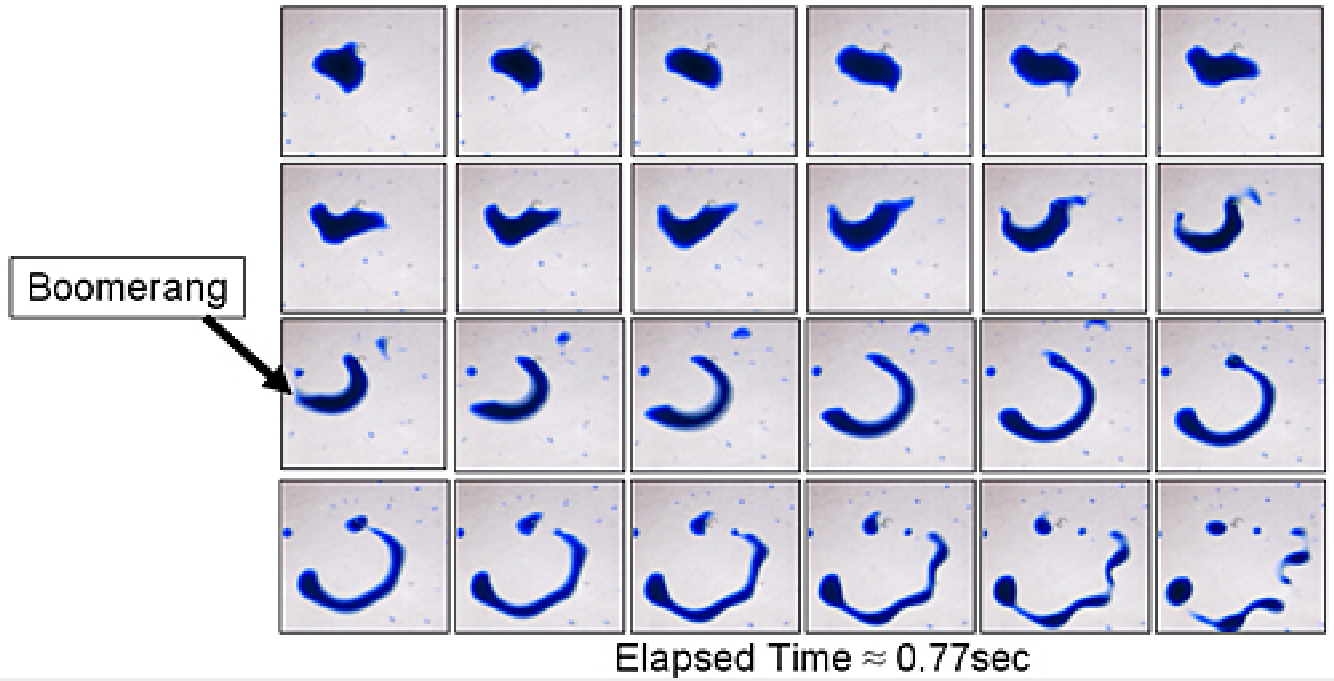
# Surface Tension Gradient Explanation of Dissolution




This illustration shows the effects of a perturbation of the liquid-liquid interface. Without an instability the drop would dissolve uniformly as on the left. However, if one side of the drop becomes indented more alcohol is dissolved into the water in region B relative to region A. This higher concentration of alcohol lowers the relative surface tension and the drop moves away from B and toward A. This continues until the molecular bonds are overcome by the surface tension gradient force. This results in the “Boomerang Breakup.”



# Boomerang Breakup




These images exhibit the major characteristics of the surface tension driven “boomerang” like dissolution of a drop of 1-octanol: the crescent-like shape in the beginning, the continued elongation of the droplet, the eventual lack of stability and integrity, and then the lysis.

# Alcohol At Lower Temperature Relative to Water

Alcohol drops at a lower temperature relative to the water they are placed on exhibit peculiar behavior. This series of pictures illustrates a drop that stays almost completely whole for a period of 3.0 seconds. This is in contrast to the room temperature drop dissolving on room temperature water that breaks up in 1 to 2 seconds at most.

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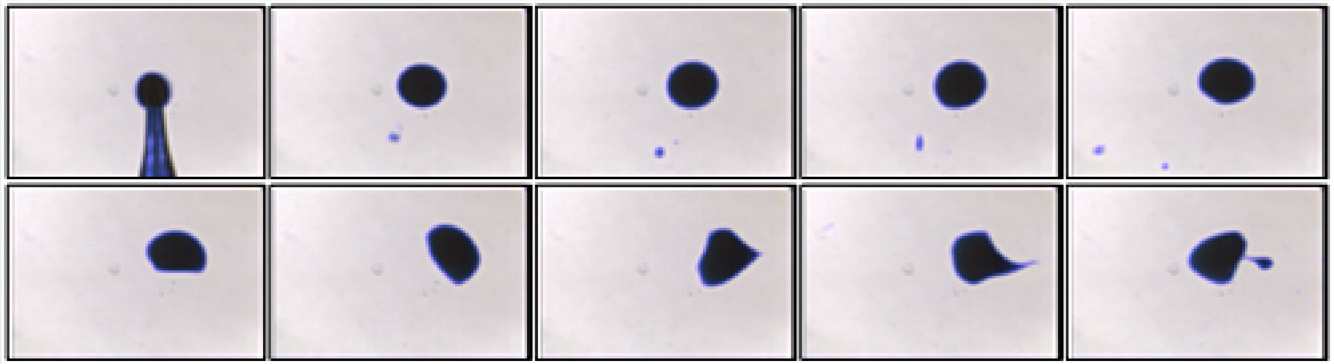
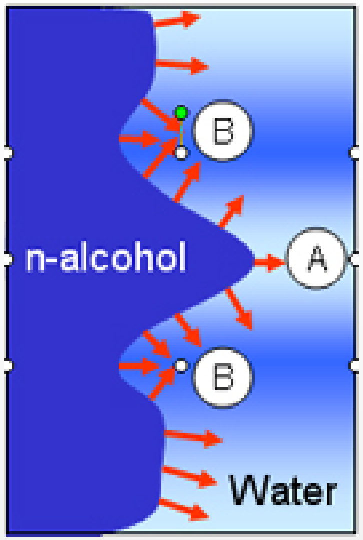
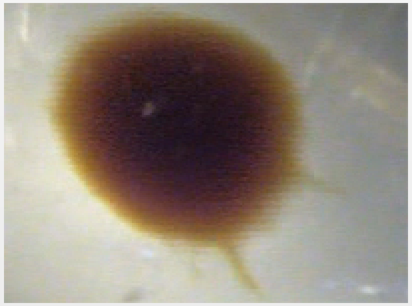


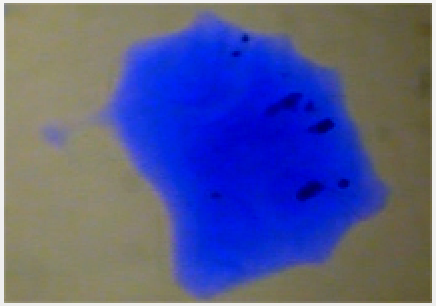
Elapsed Time ≈ 3.0 seconds

# Fingering




This figure on the left depicts the beginning of a finger. The red arrows indicate dissolution of the alcohol into the water. Region A has less alcohol per unit volume relative to B so the surface tension gradient is larger. This results in the continued movement of the protrusion outward, toward the region of higher surface tension, resulting in a finger.



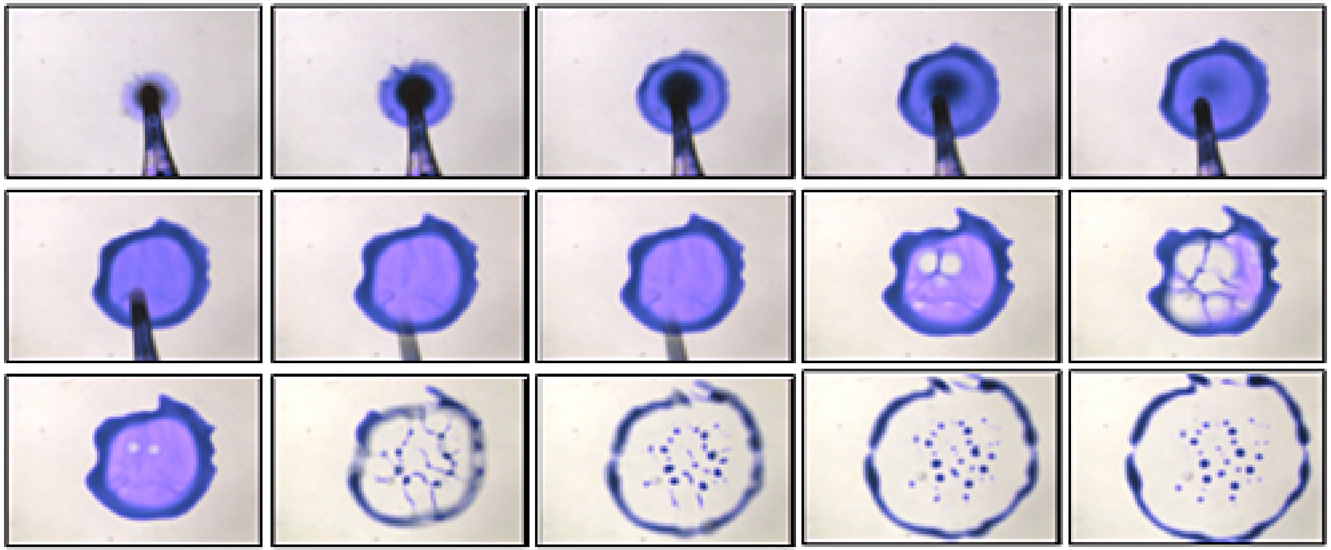


This picture on the left shows a very skinny and sharply pointed Marangoni driven protrusion, which we will call a finger. Surface tension gradient driven fingers such as this occur under particular conditions that vary between the different alcohols.

This picture on the right shows what happens when a finger protrudes far enough to overcome the molecular forces holding the drop together. When this occurs the finger "necks down", gets smaller where it is attached to the drop, and, within an average time period of one tenth of a second, separates to become its own drop.

# Alcohol at Higher Temperature Relative To Water

This is a drop of 1-heptanol at 60.0°C on 19.7°C (R.T.) water. This drop, upon contact with the water's surface, immediately spreads out to a much larger circular shape. In the middle of the circle the liquid is lighter, indicating the center is thinner relative to the rim of the drop. After ˜ 0.27 seconds the thin membrane in the middle of the drop begins to break apart, forming voids. Eventually the voids encompass the entire center of the circle and a hollow ring-like shape remains. This ring shape then breaks into many smaller drops and dissolution occurs as usual.



Elapsed Time ≈ 0.5 seconds

# Conclusions

Dealing with n-alcohols where n = 1,2,…,5 the Marangoni forces acting on the drop dominate the dissolution and overpower the cohesive forces between the molecules. This results in the drop being completely dissolved within a fraction of a second. For n = 10 and higher the molecule-to-molecule bonds of the drop mask any Marangoni forces present. It is in the intermediate range where n = 6 – 9 that the cohesive and Marangoni forces are dually expressed in the visible dissolution of the drops. It is in this range of n-alcohols that allow the drop to remain whole long enough for Marangoni forces to be observed and dissolve enough for there to be reasonable surface tension gradients. This is where the dissolution takes on such unique observable characteristics as the boomerang breakup, the divorce, and fingering.

# Applications

- Agrochemicals
- Respiratory distress syndrome (RDS)
- Mixing
- Coating
- Spraying
- Microfluidic Devices
- Biology
- Detergents
- I think you get the idea

Agrochemicals

Tears of Wine