

Development of Undergraduate Laboratory in Polymer Chemistry

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Background

It was not until 1974 that polymer chemistry began to be truly integrated into the chemistry curriculum for college students by the American Chemical Society. This delay in the development of polymer chemistry curriculum has led to a general lack of undergraduate laboratories related to the topic. The goal of this research project is to collect information about the viscosity of Pluronic F127 and use it to develop a laboratory in which students can gain a better understanding of polymer interactions in aqueous solutions.

Pluronics are triblock copolymers made of varying lengths of PEO-PPO-PEO blocks. Pluronics have been used for their surfactant properties in the development of cosmetics to help break down oils¹, or pharmaceutical purposes¹, and even for wound coverings.¹ Pluronic F127 (PEO₁₀₀PPO₆₅PEO₁₀₀) is one of the more readily available and affordable Pluronics, and easily dissolves in water with mixing and occasional heat when necessary, making it a great candidate to be at the center of this polymer laboratory.

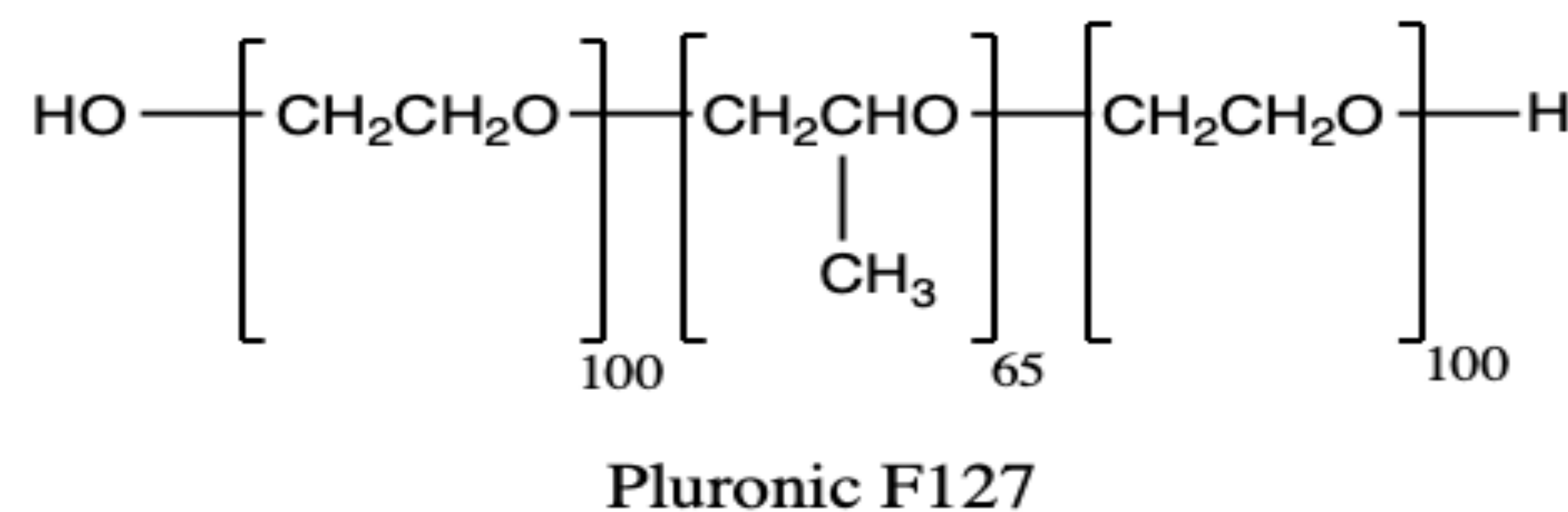


Figure 1: Pluronic F127 polymer chain.

Micelle Formation in Pluronic F127

A micelle is an aggregation of polymer molecules that maximizes water's interaction with the hydrophilic parts of the chain and minimizes its interaction with the hydrophobic parts. For Pluronic F127, the PEO blocks make up the hydrophilic exterior while the PPO block forms the hydrophobic interior of the micelle.¹

The formation of micelles in aqueous solutions of F127 can be related directly to the copolymer concentration and solution temperature. The addition of surfactants, like Sodium dodecyl sulfate (SDS), also influences the polymer's micellization abilities. There is also a correlation between micelle formation and viscosity, since the change in conformation of the polymer molecules affects how they can flow past each other in the solution. These relationships give students a connection between the macroscopic properties of the solution, and the microscopic changes of the polymer in varying conditions.

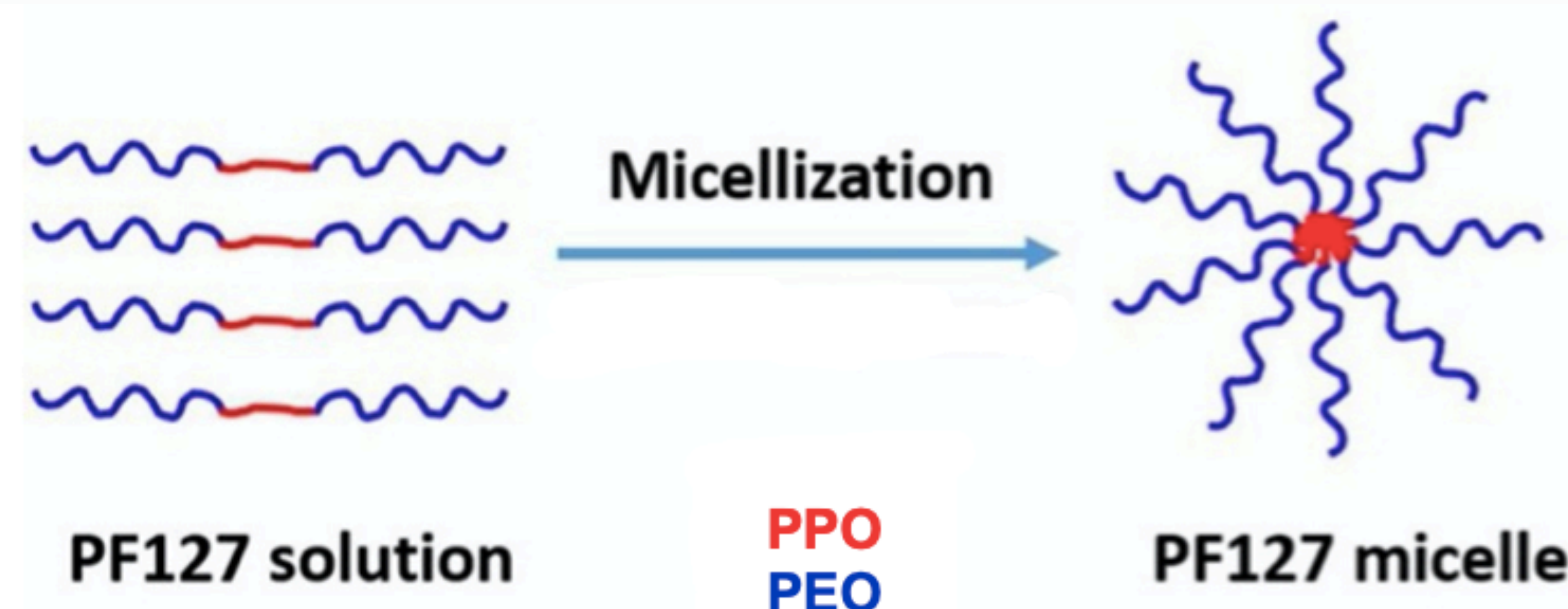


Figure 2: Visualization of PEO-PPO-PEO blocks of Pluronic F127 changing orientation to form micelles in aqueous solution (2).

Experimental

10 g/L, 31g/L, and 62g/L aqueous F127 solutions were prepared by weighing out the amount of solid F127 needed per 50mL of DI water, and dissolving in a 50mL volumetric flask. Their viscosities were measured using a 150-mL Ubbelohde viscometer at 3 different temperatures, and with the addition of SDS. Solid SDS was dissolved into the 31g/L F127 solution.

To control the the solutions temperatures, an aquarium tank with a water heater was used. The water heater kept the temperature of the water at 25°C, and 32°C, and the 22 °C temperature was when there was no water-controlled tank present. The viscometer was submerged in the water and allowed time to acclimate before measurements were taken.

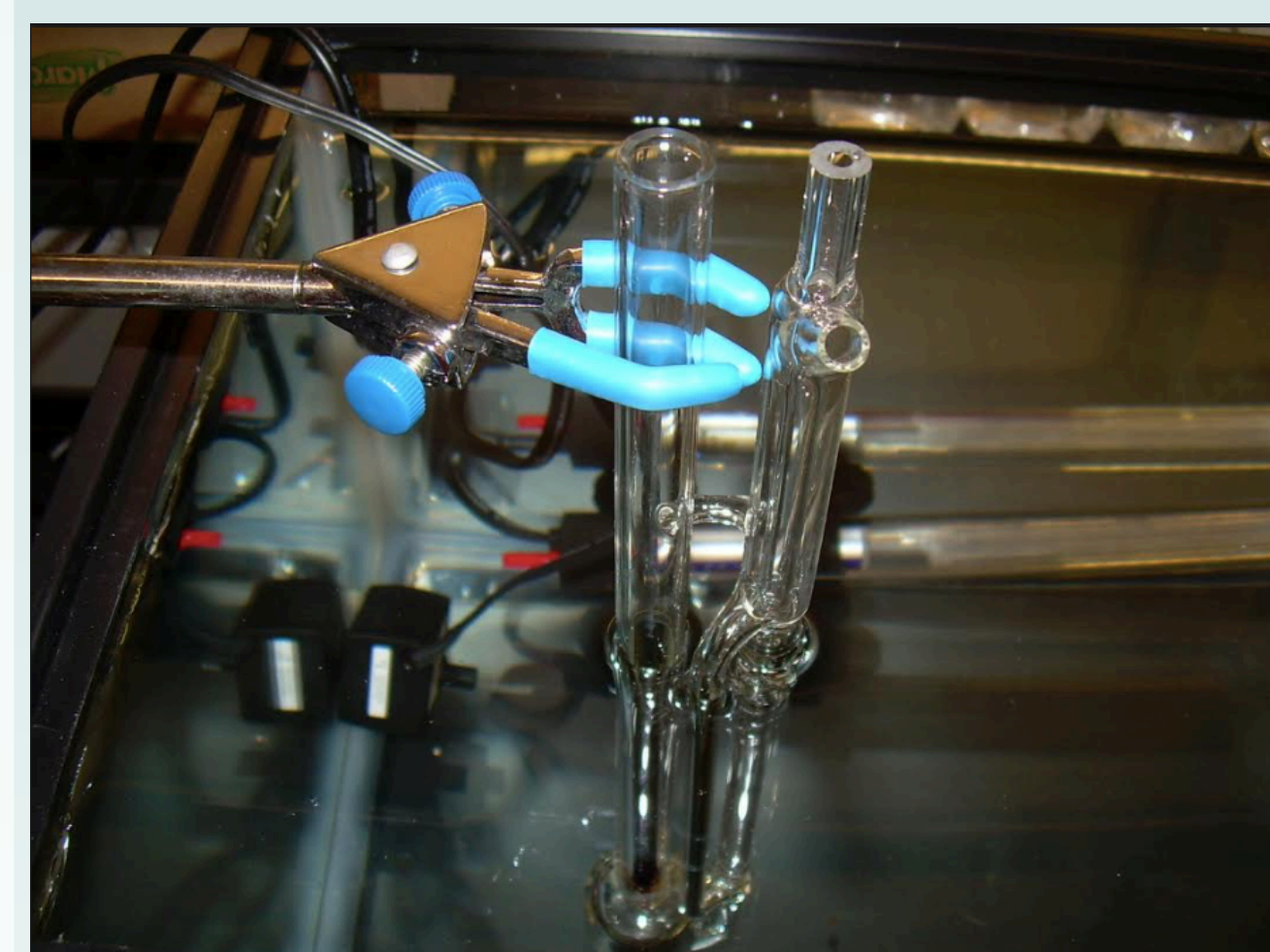


Figure 3: Set up for Ubbelohde viscometer in temperature-controlled aquarium tank.

The time that it took each solution to flow from the top mark to the bottom mark on the viscometer was then used to calculate their viscosities

t_0 = time for DI water to flow through viscometer

t = time for solution to flow through viscometer

Relative viscosity: $\eta_r = \eta / \eta_0 \sim t/t_0$

Figure 4: Formula for relative viscosity calculations.

Results

It can be interpreted from the data that as the temperatures of the solutions increase, the viscosity decreases. As the concentrations of F127 solutions increased from 10 g/L to 62 g/L, an increase in viscosity was observed. At 22 °C, a slight increase in viscosity with the addition of SDS to the 31 g/L solution can be seen when compared to the viscosity of the same concentration solution at the same temperature with no SDS added.

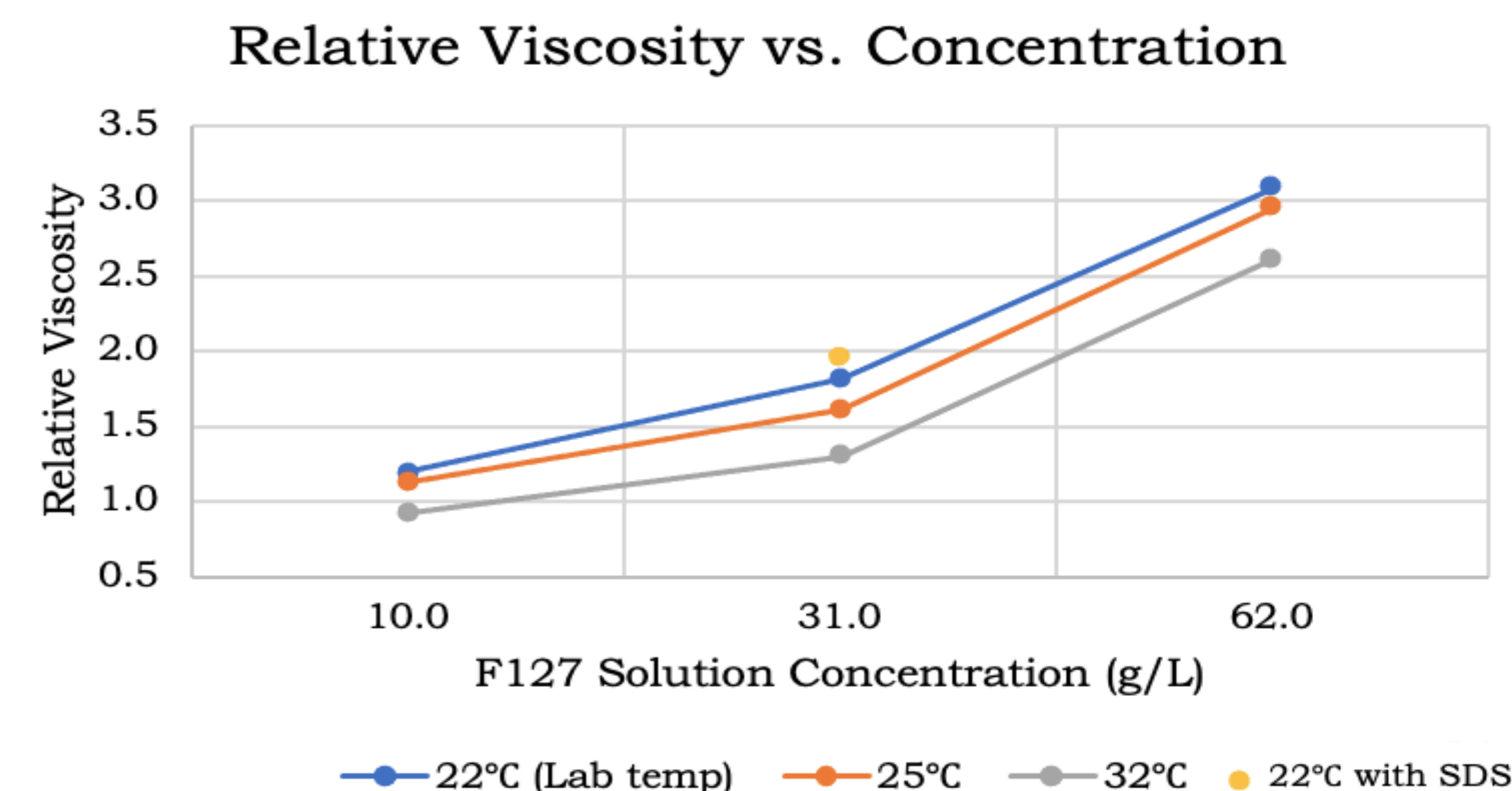


Figure 3: Relative viscosity vs. concentration graph at 22, 25, and 32°C, including data point for the 31g/L solution with SDS addition at 22°C .

Discussion

The decreased viscosity at higher temperatures may be due to an increase of micelle formation at these higher temperatures. At lower temperatures, micellization is only entropically favored, since it frees some waters from the rigid hydrogen bond network that surrounds monomers of F127, increasing entropy of the solution. This hydrogen bond network is strong and has limited mobility, but at higher temperatures, there is enough energy to break them, making the micellization process both entropically and enthalpically favored, which is probably why there is more micelle formation at these increased temperatures. The circular shape of the micelles makes it easier for them to flow, which may be why the viscosity decreases.

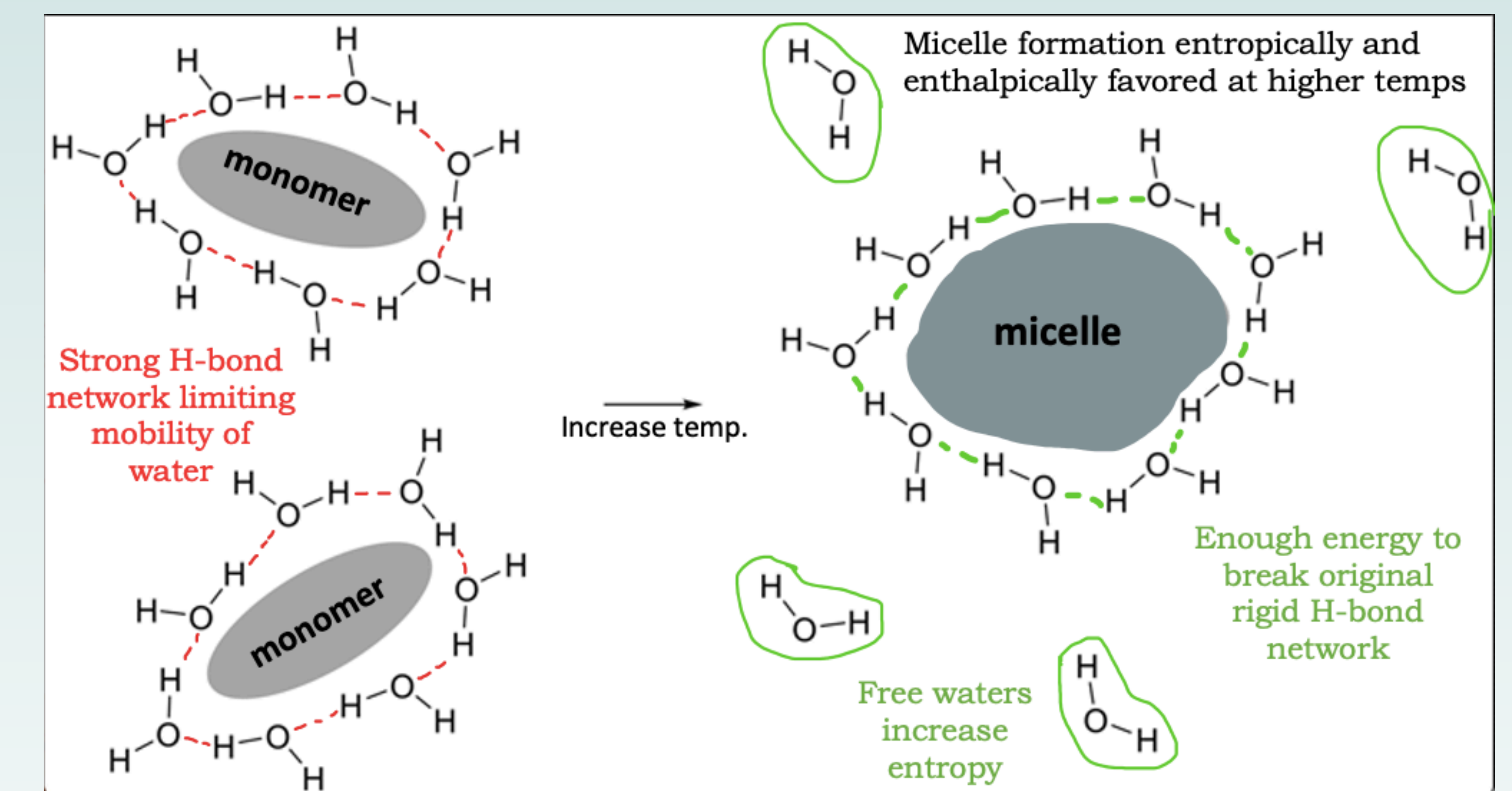


Figure 4: Visualization of the entropic and enthalpic consequences of the hydrophobic effect and the formation of micelles (3).

For increasing concentrations, there is a shift in equilibrium from the chain conformation of the F127 to the micelle conformation, so one would expect a decrease in viscosity. However, the increase that is observed may be caused by more molecules present in the solution at higher concentrations of F127, which makes it generally more difficult for them to flow past each other.

The increase in viscosity with SDS addition may have to do with how it interacts with the F127. The SDS hinders the formation of micelles. Its hydrophobic tail interacts with the PPO blocks, and its polar, charged end disrupts the PEO-water interactions, causing more molecules to be in the chain form, which do not flow as easily.

Future Work

To continue with development of an undergraduate laboratory, next steps include working with a wider range of concentrations and temperatures to see if what was predicted holds true. Surface tension measurements of the F127 solutions under these varying conditions is to be added to provide another layer to students' analysis. Also, determining the time needed to perform the full experiment will be necessary before the final paper can be submitted for publication.

References

- (1) Alexandridis, P.; Alan Hatton, T. Poly(Ethylene Oxide)□poly(Propylene Oxide)□poly(Ethylene Oxide) Block Copolymer Surfactants in Aqueous Solutions and at Interfaces: Thermodynamics, Structure, Dynamics, and Modeling. *Colloids Surf. Physicochem. Eng. Asp.* **1995**, *96* (1), 1–46. [https://doi.org/10.1016/0927-7757\(94\)03028-X](https://doi.org/10.1016/0927-7757(94)03028-X).
- (2) Raj Kumar Thapa, Flavio Cazzador, Krister Gjestvang Grønlien, Hanne Hjorth Tønnesen, Effect of curcumin and cosolvents on the micellization of Pluronic F127 in aqueous solution, *Colloids and Surfaces B: Biointerfaces*, Volume 195, 2020, 111250, ISSN 0927-7765, <https://doi.org/10.1016/j.colsurfb.2020.111250>.
- (3) Essential chemistry for biochemists - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/The-hydrophobic-effect-Water-molecules-form-an-ordered-structure-around-a-hydrophobic_fig3_320062418 [accessed 26 Apr, 2021]