Design and Evaluation of a Syringe Pump for Determining the Critical Micelle Concentration of Surfactants by Making Use of the Drop Volume Method

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ABSTRACT

Surfactants are of widespread importance in biochemistry, the detergent industry, analytical chemistry, and many other areas that are both academically and industrially important. Here we report the design and evaluation of an inexpensive and novel syringe pump. The system is suitable for the academic and small laboratory setting. It has been tested here by measuring the Critical Micelle Concentration (CMC) of surfactants with a relatively high degree of accuracy. The system may also be adapted for use in chromatography, controlled reagent dispensing for synthesis or other biochemical and biomedical applications.

I. INTRODUCTION

All surfactants share a common structural trait in that they are amphiphilic, meaning that they possess a polar end and at least one nonpolar end. This unique structure leads to many of the surfactant's unique properties. For instance, all surfactants possess the ability to lower the surface tension of water. It is this property that is commonly used to measure the critical micelle concentration of surfactants. At concentrations below the critical micelle concentration (CMC) the surfactants diffuse to the water-air, and water-container interfaces. As the surfactant concentration is increased and no more surfactant can diffuse to the water interfaces, the surfactants begin aligning themselves in spherical globular clusters called micelles. At this point, called the critical micelle concentration, any increase in surfactant concentration will no longer have any effect on the surface tension of water. This is best seen in the graph below (see Figure 1). The CMC is a very important property of surfactants which is used in various different applications. In smaller laboratories and in

Figure 1. Surface Tension of Water (mN/m).

the classroom setting the ability to measure this property was limited due to the high cost of current tensiometers which are capable of measuring surface tension of various mixtures with a high degree of accuracy, as well as other methods which require a great deal of cost [1-3]. An alternate method to directly measure the surface tension is called the drop volume method [4].

The size of an aqueous droplet is directly related to its liquid-liquid or liquid-surface interfacial tension. As surfactant is

Figure 2. Syringe Pump.

added, a decrease in the interfacial tension is seen, which then decreases the droplet size. As surfactant concentration increases, the corresponding surface tension continues to decrease until the CMC is reached. At this point any additional increase in surfactant concentration has little effect on the surface tension and droplet size remains relatively constant. The drop volume method is a direct measure of the effect of surfactant concentration on droplet size, quantified by the number of drops per a fixed volume.

At its most rudimentary level the drop volume method may employ a simple syringe to measure the CMC of a particular surfactant. However, reproducibility and accuracy are severely limited, due to the number of errors introduced by discharging the syringe by hand and counting the drops. These include tip angle, which affects the contact surface that the drop forms on, and delivery rate, which if too fast does not allow the surfactant sufficient time to diffuse to the interface. To overcome these problems, we designed and constructed the following syringe pump (see Figure 2).

The syringe pump was assembled from a 1/8" thick steel bar (vertical

attachment), motor, gearbox, potentiometer, 3/8" threaded rod, syringe, and a piston for actuating the syringe. The piston in this instance was nothing more than a hex nut welded to the top of a 3/8" tube. As the motor turns the threaded rod clockwise the piston, which is fixed to the syringe plunger, is pulled up. And as the threaded rod is turned counter-clockwise the piston is pushed downward, emptying the syringe.

II. EXPERIMENTAL

Evaluation of the syringe pump was carried out using butyl octyl dimethyl ammonium bromide, and decyl dodecyl dimethyl ammonium bromide. Delivery, or the rate at which surfactant solutions were delivered was approximately 0.2 mL/min, which corresponded to 10V for our syringe pump. Each surfactant was evaluated at 0.06 wt%, 0.05 wt%, 0.045 wt%, 0.04 wt%, 0.035 wt%, 0.03 wt%, 0.025 wt%, 0.020 wt%, 0.015 wt%, and 0.0075wt%. The collected data (drops/mL) was then plotted in *Sigma Plot 8.0* and fitted using a nonlinear regression. The critical micelle concentration was then calculated by plotting first and second derivative plots.

Figure 3. Results for Butyl Octyl Dimethyl Ammonium Bromide.

III. RESULTS AND DISCUSSION

As was expected, the decyl dodecyl dimethyl ammonium bromide had a lower critical micelle concentration (0.032wt%)

than the butyl octyl dimethyl ammonium bromide, which had a critical micelle concentration at 0.046 wt%. This was expected because as the alkyl chain length increases the cone angle of the quaternary

Figure 4. More results for Butyl Octyl Dimethyl Ammonium Bromide.

amine surfactant also increases which leads to a decrease in critical micelle concentration.

As can be seen in the graphs above (Figures 3 and 4), using the drop volume method we were able to obtain a very clear CMC for the butyl octyl dimethyl ammonium bromide. This method for building and using a simple drop volume syringe pump is very effective and also much easier and less expensive than those used in large laboratories and therefore lends itself to use in smaller laboratories and in the classroom setting. It is hoped that this tool may be used by others who have limited funds and would like to either utilize the syringe pump for surfactant studies or any of the other multitude of applications where a syringe pump can be employed [5-6].

REFERENCES

1. Lin, C., 2004. Determination of critical micelle concentration of surfactants by capillary electrophoresis. *Journal of Chromatography*. 1037 (1/2): 467-478.
2. Thorsteinsson, M., Richter, J., Lee, A., DePhillips, P., 2005. 5-Dodecanoylani-

mofluorescein as a probe for the determination of critical micelle concentration of detergents using fluorescence anisotropy. *Analytical Biochemistry*. 340 (2): 220-225.

3. Nesmerak, K., Nemcova, I., 2006. Determination of critical micelle concentration by electrochemical means. *Analytical Letters*. 39 (6): 1023-1040.
4. Castro, M., Ritacco, H., 2001. A simplified method for the determination of critical micelle concentration. *Journal of Chemical Education*. 78 (3): 347.
5. Lu, C., Wu, C., Lin, C., 2007. Protein identification by syringe pump-driven reversed phase LC-MS/MS. *Analytical Biochemistry*. 368 (2): 123-129.
6. Park, J., Koo, B., Yoon, K., Hwang, Y., Kang, M., Park, J., Hyeon, T., 2005. General synthesis of metal phosphide nanorods via thermal decomposition of continuously delivered meta-phosphine complexes using a syringe pump. *Journal of the American Chemical Society*. 127 (23): 8433-8440.