Surfactant Adsorption: A Revised Physical Chemistry Lab

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Soluble surfactants can participate in two distinct processes: (i) adsorption at interfaces and (ii) micelle or other aggregate formation. Both processes have important applications: Surface adsorption decreases the surface tension of water so that surfactants can be used as wetting agents, while micelle formation is the key to the detergency of surfactants. Both these processes are manifestations of the amphiphilic character of surfactants. However, they are distinct processes with different equilibrium constants. In this article we discuss a physical chemistry lab experiment that characterizes both processes for a nonionic surfactant.

Many physical chemistry lab courses include an experiment in which the students measure surface tension as a function of the concentration of a surface-active solute, *c,* such as methanol *(1), t*-butanol *(2),* 1-butanol *(3),* or 1-propanol *(4).* Students then graph the surface tension, γ, versus the logarithm of the concentration, to determine the surface excess, Γ, using the Gibbs isotherm equation:

$$\frac{d\gamma}{d\ln c} = -RT\Gamma \qquad (1)$$

However, the equilibrium constant for adsorption to the air–water interface is not determined in these experiments. Furthermore, these small organic molecules do not form micelles, and so students do not have the opportunity to compare the standard Gibbs energy of adsorption with the standard Gibbs energy of micelle formation. There are several published surfactant experiments in which the critical micelle concentration (CMC) is determined *(5–8).* However, these experiments do not deal with surface adsorption since the CMC is determined by other means.

We have developed a variation on CMC experiments in which students measure the surface tension of surfactant solutions. From their data they determine the molecular cross-sectional area of the surfactant molecule, the standard Gibbs energy of adsorption at the air–water interface, and the standard Gibbs energy of micelle formation. In addition, we use this experiment to introduce our students to nonlinear custom curve fitting. Nonlinear curve fitting is an important skill, in that linearization can introduce bias to the results *(9).* In our lab, the students fit the data using the solver in Microsoft Excel.

We incorporated this modified surface tension lab into our physical chemistry lab curriculum one year ago. To date, approximately 60 students have performed the modified experiment, which takes one three-hour lab period. We include student results for the most recent group of students (summer 2006).

Background

Soluble surfactants can participate in two distinct processes: adsorption at the air–water interface and micelle formation. Both these processes are manifestations of the amphiphilic character of surfactants. Below the CMC, micelles do not form, leaving adsorption as the only equilibrium occurring. The Gibbs adsorption isotherm can be rearranged to give the change in surface tension as a function of the change in concentration:

$$d\gamma = \frac{-RT\Gamma}{c}\,dc \qquad (2)$$

We can integrate this equation to get the surface tension as a function of surfactant concentration if we know the relationship between the surface excess and the concentration. If we assume that the enthalpy of adsorption is constant, this relationship is given by the Langmuir isotherm *(10)*:

$$\omega\Gamma = \frac{K_{ad}c}{1 + K_{ad}c} \qquad (3)$$

In this equation, ω is the cross-sectional area of the surfactant molecules at the surface (in m^2 per mole) and K_{ad} is the equilibrium constant for adsorption. The assumption of constant enthalpy of adsorption fails for ionic surfactants, so we use a nonionic surfactant for our experiment *(11).* Solving eq 3 for the surface excess, substituting this expression into eq 2, and integrating produces the Szyszkowski equation *(12)*:

$$\gamma = \gamma_0 - \frac{RT}{\omega}\ln\left(1 + K_{ad}c\right) \qquad (4)$$

Here, γ_0 is the surface tension of pure water. Both the cross-sectional area occupied by molecules at the surface and the equilibrium constant for surface adsorption can be determined by measuring the surface tension for different bulk concentrations of surfactant below the CMC and fitting these data to the Szyszkowski equation. The equilibrium constant for adsorption can also be used to calculate the standard Gibbs energy of adsorption:

$$\Delta_{ad}G^\circ = -RT\ln K_{ad} \qquad (5)$$

Above the CMC, surfactant molecules begin to self-assemble into micelles. Any additional surfactant molecules will be incorporated into micelles. As a result, the surface tension remains approximately constant above the CMC. Thus, the kink—an abrupt change in slope—in the surface tension curve provides a way to determine the CMC. The CMC can be used to calculate the standard Gibbs energy of micelle formation *(13)*:

$$\Delta_{mic}G^\circ = RT\ln\text{CMC} \qquad (6)$$

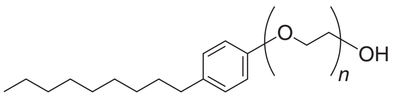

Figure 1. Igepal CO 630 was used in the experiment. The polyoxyethylene chain is polydisperse; the average value of *n* is 9.

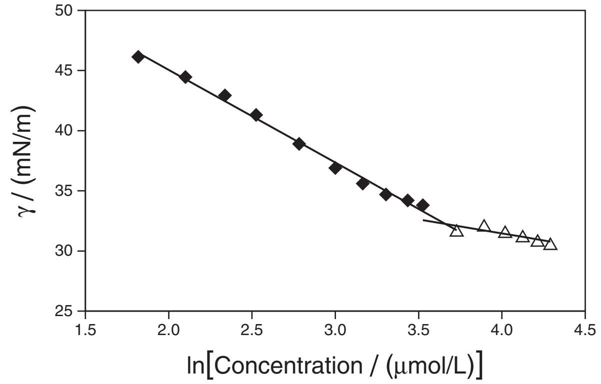

Figure 2. Surface tension as a function of the logarithm of the surfactant concentration. There is a kink in the curve at the critical micelle concentration. The lines are linear fits; the low concentration data were fit to $\gamma = -7.72\ln c + 60.5$, while the high concentration data were fit to $\gamma = -2.33\ln c + 40.8$. The CMC is the concentration at which the two lines cross. In this case, the experimentally determined CMC is 39 μM.

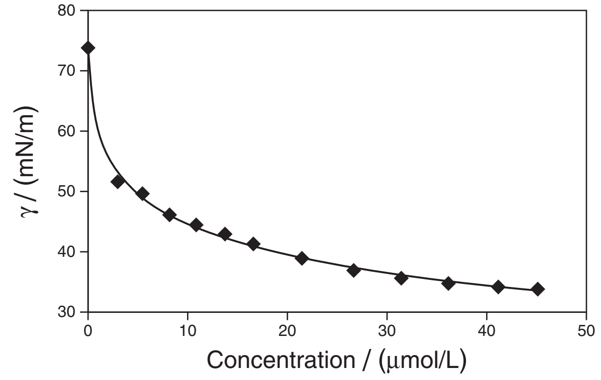

Figure 3. Surface tension as a function of the surfactant concentration. The line is a fit to eq 4, resulting in $\omega = 3.3 \times 10^5$ m^2/mol and $K_{ad} = 9.7$ μM^{-1}.

Materials and Methods

Igepal CO 630 (nonyl phenol 9 mole ethoxylate) was purchased from Rhodia Inc. and used as received (Figure 1). All solutions were made using ASTM type I (18 MΩ cm) water purified with a Nanopure system (Barnstead International, Dubuque, IA). Igepal is a viscous liquid and dissolves slowly, so the instructor prepared a working solution that was approximately 250 μM in the surfactant before lab.

The students pipet 100 mL of nanopure water into a 90 × 50 mm crystallization dish and place the dish on a stirplate. Students then measure the surface tension three times using a Nima ST9000 tensiometer with a DeNouy ring. Students use a 50 mL buret for all additions of surfactant solution. The students make six 1 mL additions, then six 2 mL additions, and finally six 5 mL additions. Each addition is followed by three minutes of stirring on a low setting (to prevent foaming), and then three readings of the surface tension. When the experiment is finished, the students measure the temperature of the solution in the dish.

Hazards

Igepal is an eye, skin, and lung irritant.

Results and Discussion

Students first plot their measured surface tension as a function of the logarithm of the surfactant concentration. An example is shown in Figure 2. The surface tension decreases linearly with concentration for the first part of the experiment, but then there is a kink in the curve. The concentration at which the line kinks is the CMC. In the example shown in Figure 2, the CMC was 39 μM. The average students value[1] for $\Delta_{mic}G°$ was −25 ± 3 kJ/mol; the literature value for $\Delta_{mic}G°$ is −24.7 kJ/mol.

After noting which data points lie below the CMC, the students fit these points to eq 4, using the solver in Microsoft Excel *(14)*. A detailed description of the fitting procedure is given in the online supplement. The students sometimes find that the solver fails to converge at the global minimum. Entering unrealistic initial values for ω or K_{ad} can result in the solver converging to a local minimum. This problem provides an opportunity for the instructor to discuss order-of-magnitude estimates for these two parameters with students. A sample result is shown in Figure 3. The average student value for $\Delta_{ad}G°$ was −40 ± 4 kJ/mol. The head group size parameter, ω, was $4 \pm 1 \times 10^5$ m^2/mol, or 60 ± 20 Å^2/molecule. There are no literature values for these parameters for Igepal CO 630 (nonyl phenol 9 mole ethoxylate). However, nonyl phenol 10 mole ethoxylate has a literature value of 3.9×10^5 m^2/mol for ω *(15)*.

The students notice that the standard Gibbs energy of surface adsorption is much more negative than the standard Gibbs energy of micelle formation. We then discuss the energetics of adsorption and micelle formation. The adsorption Gibbs energy is more negative than the Gibbs energy of micelle formation by approximately 15 kJ/mol. This makes sense, in that micelle formation is driven only by the hydrophobic effect, while adsorption is driven by a combination of the hydrophobic effect and the reduction of the surface energy of water. In fact, this can be used as a rough check on the internal consistency of the results. At saturation, the surfactants decrease the surface energy of the water by roughly 40 mJ/m^2 (see Figure 2). If we multiply this by the head group area of 4×10^5 m^2/mol, we can see that the surface energy portion of the Gibbs energy of adsorption should be 16 kJ/mol, which is roughly the difference between the Gibbs energy of adsorption and the Gibbs energy of micelle formation.

Conclusion

Modification of the traditional surface tension experiment as described in this article serves two purposes. First, it allows students to compare and contrast two distinct surfactant phenomena, micelle formation and surface adsorption. Second, it provides a context for performing nonlinear custom curve fitting. Additionally, one could further modify this experiment by using a jacketed beaker and a temperature-controlled water bath so students can perform this experiment at several temperatures. The temperature-dependent experiments would then yield $\Delta_{ad}H°$, $\Delta_{ad}S°$, $\Delta_{mic}H°$, and $\Delta_{mic}S°$.

Acknowledgments

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Note

1. All results are shown with 95% confidence limits.

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