Effect of Ionic Strength on SDS Micelle Formation

Adapted from: A. M. Halpern, **Experimental Physical Chemistry: a Laboratory Textbook, 2nd ed.**, Prentice Hall, 1997

Objective: To determine the effect of ionic strength on the self-assembly of sodium dodecyl sulfate micelles.

Background: It is well known that hydrocarbons exhibit very low solubility in water. Liquid alkanes, for example, form two-phase systems with water at almost all compositions. The fundamental reason for this behavior is summarized by the aphorism "like dissolves like". Hydrocarbons bond through weak van der Waals forces and lack the ability to engage in hydrogen bonding. Consequently, they are incapable of disrupting structure that characterizes liquid water. This fundamental incompatibility of hydrocarbons (hydrophobic) and water (hydrophilic) can be overcome if a molecule possesses both hydrophobic and hydrophilic properties. Such a molecule is called **amphiphilic** ("both sides liking"). A simple example is Ivory soap, stearic acid, which possesses a charged head group at the end of a hydrocarbon tail. Such molecules may function as detergents or surfactants (*surf*ace *act*ive ag*ents*) because they dramatically change many bulk properties of water, including its ability to solubilize otherwise insoluble compounds (i.e. dirt).

The ability of surfactants to solvate organic compounds stems from their capacity to self-assemble into monolayers, bilayers and micelles (from the Latin root *mica*, for "granule"). A micelle is an organized cluster, or aggregate, consisting of a number of monomers (~60-120). Micelles are roughly spherical in structure, having an overall diameter of ~5 nm. The interior of the micelle consists of an associated arrangement of the hydrocarbon chains of the surfactant molecules (an "oil drop"). The exterior coat of the micelle is constructed of the polar or ionic head groups. The balance between the favorable formation of the core and the unfavorable repulsion of the head groups on the surface determines to characteristics of a micellar solution, the **mean aggregation number**, $\langle N \rangle$, and the **critical micelle concentration** (CMC). In this experiment we will exam the effect of ionic strength on these two characteristics for the anionic surfactant, sodium dodecyl sulfate (SDS), $NaOSO_3C_{12}H_{25}$.

Figure 1 gives a schematic of the structure of an anionic micelle. The radius of the hydrocarbon interior is determined by the length of the hydrocarbon tail. The outer, ionic surface, which also contains associated waters of hydration, is called the Stern layer. Since anions are closely packed in this region, many are bound to their cationic counterions. Essentially, the micelle behaves like a weak electrolyte. Surrounding this ionic mantle is a region that contains both counterions and oriented water molecules called the Gouy-Chapman layer. The structure of the Stern and Gouy-Chapman layers depends on the ionic strength of the solution. As the concentration of ions in solution is increased, the charge-charge repulsion at the micelle surface is screened. Consequently, micelles can form at a lower concentration of surfactant, and the aggregation number is increased.

The hydrocarbon-like interior of the micelle gives it its many diverse and interesting properties. Because this hydrocarbon "droplet" is appreciable in size (with a diameter of ~3 nm), it has the capacity to accommodate one or more guest molecules that can undergo reactions that

are ordinarily very inefficient in aqueous media; in this sense a micelle can acts as a catalyst. We will take advantage of the property when estimating the mean aggregation number. Perhaps the most common application of micelles is as detergents, which are capable of suspending and removing soils (i.e., water-insoluble materials) from heterogeneous systems. Often Na_2SO_4 is added to increase the solvent power of the aqueous dispersion.

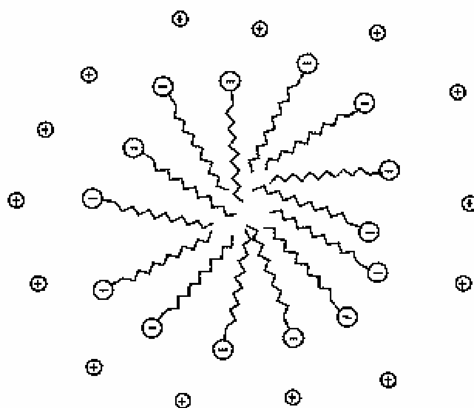

Figure 1. Schematic cross-sectional structure of an anionic micelle. The hydrocarbon chains are oriented toward the center. The solvated positive counterions surround the anionic coat of the micelle.

In the remaining discussion we will assume for convenience that a micelle is constructed of a definite **aggregation number**, N. In actuality, however, micelles must be characterized by a distribution of aggregate sizes, and so we will regard $\langle N \rangle$ as the mean aggregation number of the micellar system. In addition, we must keep in mind that a micelle is not a static entity but is constantly reorganizing itself through reversible exchanges with solvated monomeric surfactant molecules, i.e.,

$$S_N \leftrightarrow S_{N-1} + S \qquad (1)$$

Where S_N denotes the micelle constructed from N surfactant monomers, represented by S. The dynamic properties of micellar systems have been studied in detail using such techniques as temperature- and pressure- jump kinetics and NMR spectroscopy. The exchange frequency of a micelle with a monomer unit is approximately 10^3 s^{-1}; thus a micelle is restructured on the order of several times per second. It is through this process of continual, piecewise breakdown and reassembly that the micelle solubilizes hydrophobic entities such as organic molecules. The transient structure of the micelle must be taken into account when structural studies are carried out on micellar systems. Measurement techniques that take instantaneous snapshots of the structure will see static particles. Techniques that observe time-averaged properties will give a different picture.

The self-assembly of amphiphiles to form a micelle is a very complex process that appears to take place rather suddenly with respect to the addition of the surfactant to water. As was mentioned previously, micelle formation is not spontaneous until the surfactant reaches the CMC. It is a crude but reasonable approximation (valid for large N) to assume that for $[S] <$ CMC the system consists primarily of solvated surfactant monomers, while for $[S] >$ CMC, the surfactant molecules begin to assemble in micellar structures. Thus micelle formation commences when [S] ~ CMC. As [S] increases beyond the CMC, the concentration of solvated

monomers remains roughly constant (equal to the CMC), while the concentration of micelles, $[S_N]$, increases. This situation is represented in Figure 2, which shows the dependence of surfactant monomer and micelle concentration on the bulk amphiphile concentration.

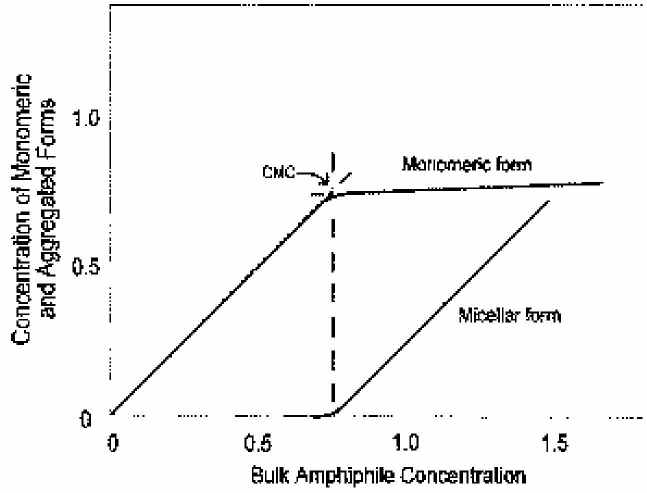

Figure 2. Concentration of monomers and micelles as a function of bulk amphiphile concentration. The monomer concentration increases up to the CMC and then levels off. Above the CMC, micelle concentration begins to build up, and the monomer concentration levels off.

The formation of micelles can be described from two very different points of view. If we consider the micelle as a well defined species (a polymer containing N monomers) we should be able to write down an equilibrium expression between monomer and aggregate. Such an expression is given in equation (2) below.

$$NS^- + mM^+ \leftrightarrow (S_N^- M_m^+)^{z-} \qquad z/N = \alpha \qquad (2)$$

Here the micelle, composed of N anions and m cations, has a negative (N-m)=z charge. The degree of dissociation, $z/N = \alpha$, represents the fraction of ionized head groups in the Stern layer. Representing $(S_N^- M_m^+)^{z-}$ by the abbreviation mic, we can write down the equilibrium constant for (2) as

$$K = \frac{a_{mic}}{a_S^N a_M^m} = \exp\left(-\Delta G^o \big/ RT\right) \qquad (3)$$

Provided the concentrations are low, the activities are nearly equal to mole fractions, $a_i \approx X_i$. ΔG^o represents the standard free energy change to make a micelle. Now we have a problem. Expression (3) implies that the micelle concentration, X_{mic}, will build even below the CMC. Here is where micellization behaves more like a phase transition than a chemical equilibrium. Just like there were water/2-butanol mixtures that were single phase, surfactant solutions are molecularly homogeneous below the CMC. Although will not predict a CMC, it can be used to represent equilibrium concentrations above the CMC. In keeping with expression (1) we will rewrite the equilibrium expression per mole of surfactant adding to a micelle of size N.

$$\Delta G^o_{mic} = \Delta G^o \big/ N = RT\left[\ln X_{CMC} + \frac{m}{N}\ln X_{M+} - \frac{1}{N}\ln X_{mic}\right] = -\frac{RT}{N}\ln K \qquad (4)$$

Here we have replaced the concentration of free surfactant with the mole fraction at the CMC. We can rearrange expression (4) to indicate how the CMC will change as a function of the cation concentration, $[M^+] = 55.5\ X_{M+}$.

$$\ln X_{CMC} = \frac{1}{N}\ln\left(X_{mic}/K\right) - (1-\alpha)\ln X_{M+} \qquad (5)$$

A graph of $\ln X_{CMC}$ vs. $\ln X_{M+}$ should be linear with a slope of 1-α. For solutions prepared with $[S]_o$ molar surfactant and $[M^+]_{salt}$ molar added cations, the total cation concentration is given by

$$[M^+] = 55.5X_{M+} = [M^+]_{salt} + CMC + \alpha\{[S]_o - CMC\} \qquad (6)$$

For solution near the CMC that have no added salt, $\ln X_{CMC} = \ln X_{M+}$. This reduces expression (4) to

$$\Delta G^o_{mic} = RT(2-\alpha)\ln X_{CMC} \qquad (7)$$

Therefore we can estimate the standard free energy of micellization from the value of the CMC and the degree of dissociation.

In this experiment you will determine the characteristic thermodynamic parameters for SDS micelles – ΔG^o_{mic}, α, <N> and K – based on a combination of solution conductivity and fluorescence quenching experiments. The conductometric method will be used to measure the CMC at various ionic strengths. A fluorescence quenching technique, that takes advantage of the catalytic effect of SDS micelles, will be used to estimate the mean aggregation number, <N>.

Conductometric Method

Pure water, as well as water containing dissolved un-ionized solutes, is a good insulator. It is the presence of charge carriers, such as mobile, solvated ions, that permits a current to flow through an aqueous solution. Thus the amount of current that flows through a sample can be used to infer the concentration of ionic species. The conductivity, κ, of a solution is proportional to the current, I, passed between two electrodes held at a potential difference, V:

$$\kappa = B(I/V) \quad \text{in } \Omega^{-1}\text{cm}^{-1} \qquad (8)$$

where B is a constant that depends on the characteristics of the experimental apparatus.

The basic approach considered in this experiment is as follows: below the CMC, the addition of amphiphiles causes an increase in charge carriers - Na^+(*aq*) and $–OSO_3C_{12}H_{25}$(*aq*). Above the CMC, further addition of surfactant results in an increase in micelle concentration while the monomer concentration remains approximately constant (at the CMC level). The intrinsic conducting property of a surfactant monomer, such as its diffusional mobility, is very different from that of a micelle; in fact, it can be expected that the ionic mobility of the monomer is larger than that of the micelle. A series of measurements of κ vs. surfactant concentration should therefore give rise to a change in slope near the CMC, with a smaller slope occurring after the CMC has been reached.

The concentration dependence of the ionic conductivity is given by Kohlrausch's law:

$$\kappa = \frac{C\Lambda}{1000} \qquad \Lambda = \Lambda^o - \beta\sqrt{C} \qquad (9)$$

Here C represents the concentration of positive (or negative) charge in solution (the normality expressed in mol/L) and Λ is the equivalent conductance (expressed in $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$). The

limiting equivalent conductance, Λ^o, is generally represented as a sum of the contribution from an equivalent of each ion in solution, λ_i. These values are available in standard handbooks. As an example, consider Λ^o for the Na_2SO_4(*aq*).

$$\Lambda^o = \lambda(Na^+) + \lambda(SO_4^{2-})/2 = 50.1 + (160.0)/2 = 130.1\ \Omega^{-1}\ cm^2\ mol^{-1}$$

Expression (9) indicates that a graph of κ vs. C should give a line with a gently decreasing slope. The trick with this experiment is to distinguish the gentle slope change from the "abrupt" change that occurs at the CMC.

Fluorescence Quenching Technique:

Let us consider an aqueous solution of a surfactant that has a bulk concentration, $[S]_o$, which is above the CMC. If we make the simple assumption that the surfactant molecules are present either as monomeric units or as micelles that contain N monomers, there will be a concentration of such micelles, [M], which can be expressed as

$$[M] = \frac{[S]_o - CMC}{N} \qquad (10)$$

where *CMC* is the concentration of free monomers in solution. Because the numerator in equation (10) can be directly determined (the CMC can be obtained from conductivity measurements), we could find the value of N if we knew the average micelle concentration in the system. In this experiment, we will use a fluorimetric technique to measure $\langle N \rangle$.

The method involves several simple but important assumptions:

1. A luminescent probe molecule is added to the micelle system. This probe is exclusively associated with (i.e., dissolved in or bound to) a micelle rather than being dispersed in the aqueous medium. The luminescence intensity of the system is then proportional to the fraction of "tagged" micelles (not all micelles have a probe in them).

2. There are many more micelles present than probe molecules. Thus only a fraction of the micelles present contains the probe molecules; a micelle is either empty or associated with a probe molecule.

Suppose a luminescence quencher is added to this system. The quencher essentially removes the photoexcitation energy from the probe, so the probe does not luminesce after it absorbs light. Our assumptions continue:

3. The quencher is associated with micelles only; it is not solvated in the aqueous medium.

4. These solubilized quenchers occupy micelles randomly, irrespective of whether they are vacant or occupied by a luminescent probe molecule.

5. If a probe shares a micelle with one or more quenchers, the probe will not luminesce.

The following is another important methodological requirement. The micelle is continually exchanging monomers with the solvent (at a rate of roughly several thousand times per second) whereby it undergoes a complete reorganization tens of times per second. Therefore a probe being used to determine its mean aggregation number (a static concept) must "take a snapshot" of the micelle on a time scale of much less than -1-10 ms. Luminescent probes easily satisfy this criterion because their intrinsic lifetimes are usually less than 1 μs.

The luminescence intensity of the system is proportional to the number of micelles that occupy a probe molecule but no quencher. Thus for a particular (bulk) quencher concentration, the ratio of the luminescence intensity, I, to that when no quencher is present, I^o, (the bulk probe concentration being constant) is equal to the fraction of probe-containing micelles that do not contain a quencher molecule.

We now consider the statistics of such a situation. If q quenchers are placed randomly in m micelles, the distribution of these quenchers in the micelles is governed by Poisson statistics (if q and m are large). Such a distribution means that the probability of finding n quenchers in a randomly selected micelle is given by

$$P_n = <q>^n \frac{\exp(-<q>)}{n!} \qquad (11)$$

where $<q>$ is the overall probability that a micelle contains at least one quencher, i.e., $<q> = q/m$. Macroscopically, $<q>$ = [Q]/[M], where [Q] is the bulk quencher concentration and [M] is the (mean) micelle concentration. Of particular interest to us is the probability that a micelle contains no quencher, because if such a micelle contained a probe, it would produce luminescence. Thus we have from equation (11), where $n = 0$,

$$P_o = \exp(-<q>) = \exp(-[Q]/[M]) \qquad (12)$$

(Remember O! = 1.) Finally, we relate the measured quantity I/I^o to the fraction of quencher-unoccupied micelles:

$$\frac{I}{I^o} = \exp\left(-\frac{[Q]}{[M]}\right) \qquad (13)$$

Recapping, I^o is the luminescence intensity of the probe-containing surfactant system in the absence of quencher. It is proportional to the number of micelles containing a probe. I is the luminescence intensity in the presence of Q moles per liter of quencher, and it is proportional to the number of micelles containing a probe, but *without* a quencher.

Substituting the expression for [M] from equation (13) into equation (10) and rearranging, we have

$$\ln\left(\frac{I^o}{I}\right) = \frac{[Q]<N>}{[S]_o - CMC} \qquad (14)$$

We can use equation (14) to determine <N>, knowing the *CMC* from conductance measurements. A measurement of $\ln(I^o/I)$ vs. [Q] should yield a linear relationship from which <N> can be obtained.

Experimental:

Reagents:
- Sodium Dodecyl Sulfate
- Sodium Sulfate
- Tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate
- Absolute Ethanol
- 9-Methylanthracene
- Deionized Water

Apparatus: YSI Conductivity Meter
Perkin Elmer LS50B Fluorimeter
250 mL Graduated Cylinder
1 mL Volumetric Pipet
1 250 mL Volumetric Flask
2, 100 mL Volumetric Flask
1 10 mL Volumetric Flask
Constant Temperature Bath
Magnetic Stirrer
2 Lab Jacks
Closed Fluorimeter Cells
Aluminum Foil

Procedure: **Conductivity Measurements**

1) Prepare 100 mL of a 0.03 M SDS solution in deionized water.
2) Set up the constant temperature bath on the two lab jacks such that the magnetic stirrer makes contact with the bottom of the bath.
3) Place the 250-mL graduated cylinder in the bath directly above the magnetic stirrer. Add 100 mL of deionized water to the cylinder and place a magnetic stir bar in the cylinder to be sure it turns.
4) Add water to the constant temperature bath and stabilize the temperature at 30 ^{o}C.
5) Keep the flask containing solution A in the constant temperature bath to equilibrate it at 30 ^{o}C.
6) Attach the conductivity cell to the back of the conductivity meter. Set the display to read conductivity.
7) Thoroughly rinse the conductivity cell with deionized water. Place the rinsed cell into the graduated cylinder, turn on the magnetic stirrer for a minute, then with the magnetic stirrer turned off record the conductivity and temperature of the deionized water in the cylinder. This is your baseline reading.
8) Add 2 mL portions of the SDS solution to the cylinder, mix for a minute, and record the conductivity and the temperature.
9) Continue step (7) until all of the SDS solution has been used.
10) Repeat the conductivity experiment, replacing deionized water with a 0.01 M sodium sulfate solution (both as the SDS solvent and as the initial solution of step 3).

Fluorescence Measurements

Solution A: Prepare 10 mL of a 3.0×10^{-3} *M* 9-methylanthracene solution in absolute ethanol.

Solution B: Prepare 250 mL of an aqueous solution containing 7×10^{-5} *M* tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate and 0.02 *M* SDS.

Solution C: Add 2 mL of solution A to a 100 mL volumetric flask. Fill the flask with solution B. This is the quencher solution.

Solution D: Fill a 100 mL volumetric flask with solution B.

1) Familiarize yourself with the use of the fluorimeter. Set the temperature controller at 30 ^{o}C.
2) Add 3 mL of solution D to one of the closed fluorimeter cuvettes. Optimize the emission spectrum of $Ru(bipy)_3$ by setting the emission maximum to ~900. This should be your largest emission line. Save this cuvette for reference purposes.
3) Add 2 mL of solution C to the flask containing solution D. Mix well, then transfer 3 mL of the solution into the other fluorimeter cell. Place the cell in the fluorimeter and allow the temperature to equilibrate (~ 5 min.) Record the emission spectrum.
4) Discard the contents of the cuvette used in (3) in the organic waste.
5) Repeat steps (3) and 4) until the signal stops changing, or you run out of solution.
6) Record the reference spectrum again after you're done with the solution series. This will enable you to detect drift in the instrument.

Analysis:

1) For the two solutions tested with the conductivity apparatus, make a table of the raw data – volume added, temperature and conductivity.
2) From the data in step (1) determine the molarity of SDS in each solution and adjust the conductivity by

$$\kappa_{adj} = \kappa \exp\left(\frac{16500}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right) - \kappa_o$$

where κ_o and T_o refer to the conductivity and absolute temperature of the baseline reading. This correction accounts for the fact that conductivity depends on solvent viscosity.

3) Make a plot of κ_{adj} vs. molarity of SDS for the two conductivity series on the same graph.
4) Generate regression lines through the high and low molarity regions of the curves in step (3). The intersection of these lines is the CMC. Report these values along with an estimate of their 95% confidence intervals.
5) Estimate the degree of dissociation, α, using expression (5).
6) Estimate the value of ΔG^{o}_{mic} using equation (7) with the value of α from step 5.
7) Make a table of the raw data of the fluorescence experiment – experiment # and intensity at the emission maximum.
8) From the data of step (7), determine the molarity of 9-methylanthracene, the quencher. Call this [Q]. Adjust the emission intensity for any drift that may have occurred between the first and last measurement. Assume this drift to be linear in time.
9) As indicated in equation (14), make a plot of $\ln(I^{o}/I)$ vs. [Q]. Here I^{o} is the intensity at the emission maximum without quencher present. From the slope and the CMC determined in (4) calculate the value of the mean aggregation number, <N>. Give an estimate of its precision.
10) Determine the equilibrium constant, K, using equation (4).