

Experiment 4

Mixing the Unmixable: Surfactants in Solutions, Emulsions and Lotions



The Task

The goal of this experiment is to produce an appealing lotion using the minimum concentration of NaHCO_3 .

Skills

At the end of the laboratory session you should be able to:

- make up a series of diluted samples,
- accurately weigh out samples,
- clearly and accurately record data in your logbook,
- interpret a graph.

Other Outcomes

- You will observe how surfactants can solubilise oil in water.
- You will observe the instability of emulsions and the factors that influence it.
- You will observe the effect of pH and metal cations on the behaviour of a surfactant.
- You will prepare a lotion.
- You will understand the role of each ingredient in the lotion preparation.

The Assessment

You will be assessed on your ability to use a top-loading balance. (See Skill 3.1) This includes all associated aspects such as replacing lids on reagent bottles, avoiding contamination of reagents, cleaning up spillages (if any) and recording masses correctly in your logbook.

Introduction

The simple division of the states of matter into gases, liquids and solids runs into a problem when confronted by *goo*. Gels, slime, lotions, creams, pastes, mucus and grease are familiar materials that exist somewhere between liquids and solids. They can often retain a shape like a solid but can also be made without much effort to flow like a liquid; hence their common classification as ‘soft matter’.

In the two huge fields of food science and cosmetic science, the problem of controlling the texture of a preparation is of central importance. A shampoo that cannot be held in your palm without flowing away is difficult to use. Ice cream that contains large ice crystals rather than a smooth creamy texture will not be popular.

One basic feature that all of these soft materials have in common is that they are mixtures of a number of components and, in general, not very good mixtures. By this we mean that there is some degree of separation into the pure components. The inability of oil and water to mix is a very familiar example of this tendency to separate. Milk, butter and mayonnaise are substances whose distinctive properties arise as a result of the special balance that has been struck between mixing and separation of fats and water. The opaqueness of milk, for example, is due to the presence of small globules of fat and protein that scatter light rather than let it pass through the liquid. A small adjustment of the chemical composition can dramatically shift this balance and result in a large change in a mixture’s properties. Consider the curdling of milk by a squeeze of lemon.

In this experiment you will explore these strange states of matter by working out how to build them, step by step, from simple chemical components. To do this, let’s look at the properties of sodium sulfate and sodium dodecylsulfate (SDS).

Sodium sulfate, Na_2SO_4 , is an ionic crystalline compound that dissolves in water to give $\text{Na}^+(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ ions.

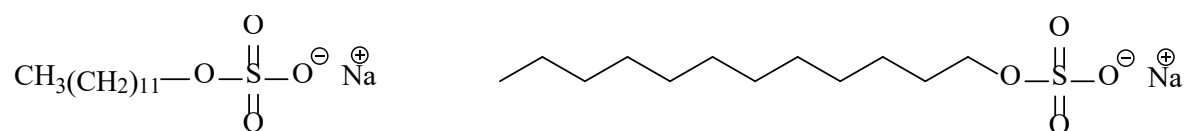


Figure 1. The structure of sodium dodecylsulfate (SDS)

In subsequent figures we have just used stick notation, a shorthand method of drawing complex organic molecules. The lines represent bonds and, unless otherwise specified, the atoms at the ends of all bonds are carbon. Whenever a carbon atom has fewer than 4 bonds, the number of hydrogens bonded to it can be calculated - carbon always has a valence of 4 and the undrawn bonds are assumed to be bonds to hydrogen.

Solid sodium sulfate dissolves readily in water at room temperature. SDS is also an ionic compound, so we might expect it to dissolve in water also. On the other hand, the long hydrocarbon chain of SDS resembles dodecane, a non-polar molecule with very little solubility in water. What will happen when SDS is added to water?

SDS does dissolve in water but, as the concentration of SDS increases, it tends to cluster in clumps known as *micelles* (see Figure 2). In a micelle, the non-polar tails of the molecules are all buried in the middle of the cluster, away from the water, while the polar or charged head groups are on the cluster surface, exposed to the water.

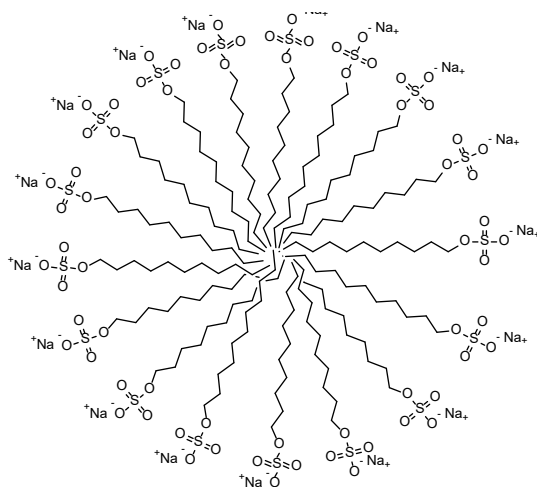


Figure 2: SDS micelle showing the non-polar core and a polar surface. Micelles are spherical, not circular as suggested by the above 2-D diagram.

Useful Terminology

Molecules like SDS have some distinctive and useful properties – clustering with itself and solubilising oil – and, as a result, have ended up with a number of names. Here are some names and their definitions.

Amphiphile: An amphiphile is a molecule consisting of a hydrophobic (“water-hating”) part (*i.e.* non-polar) and a hydrophilic (“water-loving”) part (*i.e.* polar or charged) so that they are soluble in both water and non-polar organic solvents.

Surfactant: A surfactant is an amphiphile that lowers the surface tension of a liquid, allowing it to spread on a surface. Most amphiphiles are also surfactants.

Soap: A soap is a surfactant consisting of a salt of a fatty acid, usually with sodium or potassium as the cation.

Detergent: A detergent is a surfactant that is used for cleaning, particularly the removal of grease. Although they have similar behaviour, soaps are not usually included as detergents.

Emulsion: A mixture of a polar and a non-polar liquid (*e.g.* water and oil). With time emulsions tend to separate into polar and non-polar phases.

Emulsifier: An emulsifier is a substance, often a surfactant, that stabilises an emulsion, *i.e.* prevents it from separating.

Concentration Scales

The concentration of a solution can be specified in a number of ways. The table below gives definitions of the different types of concentration.

Name	Symbol	Definition
molarity	M	number of moles of solute per litre of final solution
molality	m	number of moles of solute per kg of solvent
mole fraction	X	number of moles of compound divided by total number of moles of solvent and solute present.
percentage weight of total volume	% (w/v)	number of grams of added material (either solid or liquid) per 100 mL of final solution
percentage volume of total volume	% (v/v)	number of mL of added material (usually liquid) per 100 mL of final solution
percentage weight of total weight	% (w/w)	number of grams of added material (either solid or liquid) per 100 g of the final solution

The concentration scales of % (w/v), % (v/v) and % (w/w) have the advantage that you don't need to know the formula weight of the added material to calculate the concentration. They're often used when the formula weight of the added material isn't known, or, even when the formula weight is known, simply for the sake of convenience.

Safety

Chemical Hazard Identification

sodium dodecylsulfate (SDS) – irritant. Avoid eye/skin contact and dust inhalation.

canola oil – non-hazardous

eicosane (candle wax) – combustible, irritant

stearic acid – low toxicity, irritant, combustible

sodium hydrogencarbonate – non-hazardous, low toxicity, low irritant

0.1 M magnesium nitrate – non-hazardous, corrosive - irritant

0.1 M aluminium nitrate – hazardous, corrosive – irritant

0.1 M sodium nitrate – non-hazardous.

0.1 M nitric acid – non-hazardous, corrosive. Avoid eye or skin contact.

Risk Assessment and Control

Low risk

Solid SDS is an irritant - take care to avoid inhalation of the dust when weighing it and making up solutions.

Take care with the hot plates. Don't accidentally burn yourself.

Waste Disposal

Preparations containing oils and solids must be placed in the waste container provided. All other waste **solutions** from this experiment can go down the sink.

Experimental

This experiment is to be carried out in pairs.

Part A Effect of pH and metal cations on emulsion stability

How does changing the pH of the solution affect the emulsion stability? Does the addition of a metal cation affect the emulsion stability? To find out you are going to make an oil and water emulsion and then test the emulsion.

- (A1) In a 250 ml beaker make 100 mL of a 5 % w/v stock solution of SDS in deionised water for use in this and subsequent experiments.
- (A2) Take 21 mL of your 5 % SDS solution in a 250 mL beaker and dilute with 21 mL of deionised water. Add 25 mL of canola oil and stir vigorously for 1 minute, being careful not to make lots of bubbles. In your logbook, describe what the mixture looks like. You have formed an emulsion, *i.e.* oil droplets dispersed in water, stabilised by surfactant (SDS).
- (A3) Carefully use a plastic dropper to transfer approximately the top 1 cm of the emulsion that has formed in the top layer from step (A2) to a test tube.
- (A4) Immediately add 1 mL of 0.1 M $\text{Mg}(\text{NO}_3)_2$ to the test tube and mix by shaking the test tube from side to side. Leave the test tube to stand in the test tube rack.
- (A5) Repeat steps (A3) and (A4) with the following solutions:
- 0.1 M $\text{Al}(\text{NO}_3)_3$
 - 0.1 M NaNO_3
 - 0.1 M HNO_3
- (A6) When you have finished, observe the contents of the test tubes more closely by carefully pouring them onto a watch glass and placing it on a black tile. **Record your observations in your logbook.**

For your logbook:

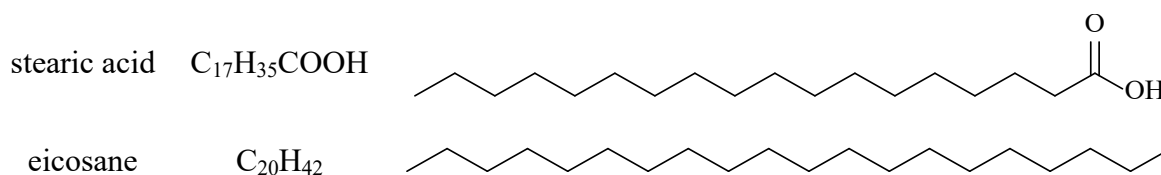
For the samples where you could see that the emulsion was destroyed, i.e. you could see oil and water separate, what do think happened to the SDS?

Part B Preparations: Assembling a Lotion

One route to slowing down the separation of an emulsion is to solidify the oil phase. This strategy, as we shall see, has the interesting effect of turning a milky liquid emulsion into a shiny semi-solid lotion. There are two extra ingredients required in addition to water, oil and SDS to make a lotion and we will introduce them one at a time.

The first ingredient we need is a chemically inert, biologically safe, low melting point solid. Stearic acid is found in many animal fats and vegetable oils, especially cocoa. Eicosane is a constituent of paraffin wax (long unbranched alkanes) and is used to make candles. Both of these compounds fulfil all of our requirements.

Your demonstrator will assign you stearic acid or eicosane.



- (B1) Take 3 g of stearic acid OR candle wax (eicosane) in a clean dry 250 mL beaker (Skill 3.1B) and add 12 mL of canola oil. Place the beaker on a hot plate stirrer and stir until all of the solid material has melted (do **not** boil the solution).
- (B2) Add 42 mL of deionised water to the oil mixture and stir briefly, then carefully use tongs to remove the beaker from the hot plate.
- (B3) As the mixture cools, record in your logbook what you observe. Observe what happened when the other compound was used (from a neighbouring group).
- (B4) Repeat steps (B1) - (B3) using the same compound, but instead of using water, use 42 mL of the 5 % w/v SDS in water solution made in step (A1).
- (B5) Again record in your logbook your observation of the mixture as it cools. Don't throw away the samples. You need to check on them after 10 and 20 minutes and record your observations.

For your logbook:

The stearic acid and eicosane solidify as they cool. From your observations, what is happening to the oil phase in which the stearic acid or eicosane resides?

The second (and last) ingredient we need to make a lotion is sodium hydrogencarbonate, NaHCO_3 . This compound is found in most kitchens and is sold in supermarkets under its old name of sodium bicarbonate (or bicarb of soda or baking soda). Let's see what this simple salt does and why we add it. You are going to repeat the procedure (B1) - (B5), but this time including some HCO_3^- ions in the aqueous solution.

- (B6) Take 3 g of stearic acid OR candle wax in a clean dry 250 mL beaker (Skill 3.1B) and add 12 mL of canola oil. Place the beaker on the hot plate and stir until all of the solid material has melted (do **not** boil the solution).
- (B7) Weigh out 3 g of SDS in a clean dry 250 mL beaker (Skill 3.1B) and add 42 mL of 5 % w/v NaHCO_3 solution. Warm this on the hot plate and stir gently (so as not to produce bubbles) until all of the SDS has dissolved (do **not** boil the solution).
- (B8) Add the NaHCO_3 mixture to the oil mixture and stir briefly, then carefully use tongs to remove the beaker from the hot plate.
- (B9) As the mixture cools, record in your logbook what you observe. Also observe from a neighbouring group what happened when the other compound was used.

For your logbook:

Compare the appearance and properties of your three samples. (When cool, it's safe to poke this stuff with your finger):

Sample 1. oil + water + stearic acid or candle wax

Sample 2. oil + water + stearic acid or candle wax + SDS

Sample 3. oil + water + stearic acid or candle wax + SDS + NaHCO_3

Part C A lotion relies on solidified particles

In some of the 3 samples you prepared in Part B, the presence of a solid phase is obvious, but in others, particularly those resembling lotions, it might not be so clear. One simple test is to see what happens if you heat a mixture above the melting point of the solid component, stearic acid (67 - 72 °C) or candle wax (36 - 38 °C).

- (C1) Place a beaker containing your Sample 3 from the previous exercise (*i.e.* the sample with SDS and NaHCO_3) onto the hot plate.
- (C2) In your logbook, record your observation as your sample is heated. Also observe from a neighbouring group what happens when the other solid component is used.

Part D Developing your preparation

By now, you should have observed how it is possible to adjust the properties of a mixture by adding various chemical species. Many consumer materials consist of carefully worked out preparations, in which the choice of components and their concentrations have been adjusted to optimise the desired properties. Commercial lotions, for example, typically include mixtures of oils, preservatives, scent and a variety of surfactants.

In this exercise you have to make an appealing lotion (*i.e.* shiny smooth texture, stiff and stable against separation) using the minimum amount of NaHCO_3 . For the sake of this exercise, the composition of oil : aqueous phase : SDS is fixed at 12 mL : 42 mL : 3 g, but you can experiment with different amounts of stearic acid (up to 3 g) and NaHCO_3 (up to 5 % w/v). The NaHCO_3 is available at 5 % w/v; you need to dilute this solution (Skill 4.5) to make up any other NaHCO_3 concentrations that you may require.

- (D1) Devise a plan of the various compositions that you will test. Use no more than 4 different compositions. Using a grid or matrix might help (an example is given in Figure 3). Remember you would like to focus your testing on composition ranges where success is likely, so think about the compositions that you might exclude. All dilution calculations must be neatly recorded in your logbook. After you have mixed your different compositions, you can cool them on ice.
- (D2) Record in your logbook your testing plan and the composition and outcomes for each of your test samples. Select from your test samples the one that best meets the goals of producing a good lotion using the **minimum** concentration of NaHCO_3 . Submit your selected sample, along with the amounts of stearic acid and sodium hydrogencarbonate used, to your demonstrator. Your demonstrator will determine the group winner.

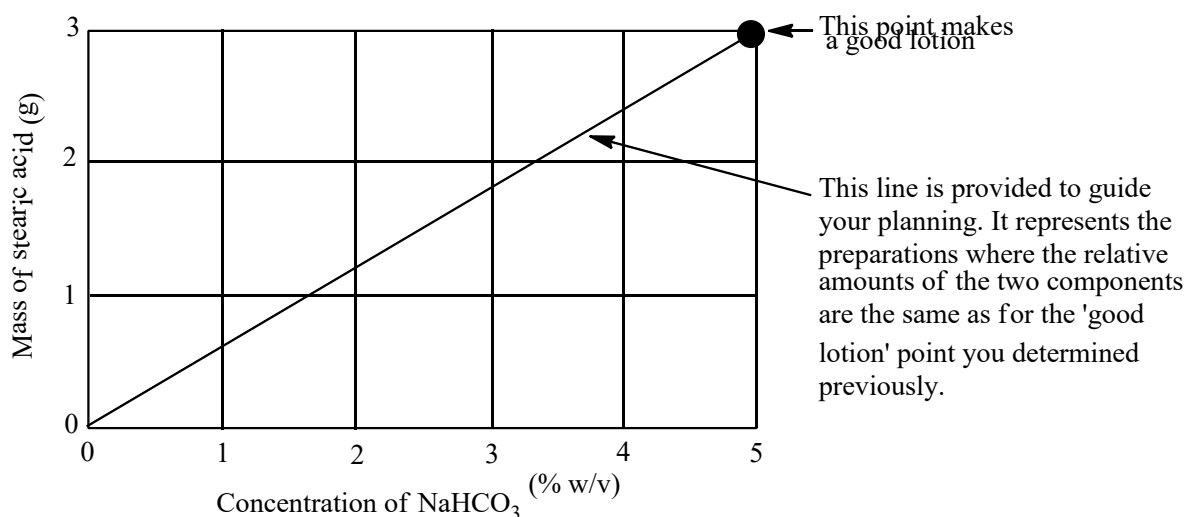


Figure 3: Each possible preparation is a point on this grid.

Group Discussion

Can you explain the effects of metal ions and acid on the emulsion stability that you observed in Part A?

In part B, which solid formed a better lotion, stearic acid or eicosane?

What role do you think HCO_3^- ions are playing in the preparation of a lotion?

Based on your experimental results, can you suggest a reason why clay particles are deposited and silt up river deltas?