

# Practical Chemistry of Long-Lasting Bubbles

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**Abstract** In this report, an experiment is described in which high school students investigate long-lasting bubbles of their own design. The features of the soap bubbles change depending on their chemical composition. To investigate the students' original bubbles, the chemical structures and features of the ingredients are considered when choosing the detergent, polymer, and other chemical components. Soap bubble containing sucrose, sodium alkyl ether sulfate (AES)-detergent and poly(vinyl alcohol) (PVA) (or partially hydrolyzed poly(vinyl alcohol) (PVAAc)) often maintains a spherical shape on various solid surfaces, including concrete, asphalt, tile, and grass after landing. Students hypothesize that the low surface tension of the long-lasting bubble is not the sole reason for its long lifetime on various solid surface. The mechanism behind the extended lifetime is discussed through experiments involving the surface tension and lifetimes of the bubbles under various humidity conditions. Students encounter basic chemistry through the experiment, which can be adopted into the chemistry curriculum.

**Keywords:** long-lasting bubble, polymer, surfactant, high school chemistry

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## 1. Introduction

A soap bubble can be used as an effective teaching aid to explain various interesting scientific problems to high-school chemistry students. As a chemical problem, many studies have investigated surfactant [1] and polymer [2] compositions that can be used to stabilize bubble films so as to obtain "long-lasting" or "giant" soap bubbles. A mathematical problem known as "Plateau's problem," which indicates the existence of an area with the minimal surface for a given boundary, can be solved using a soap film [3]. In terms of physics, the mechanism of stabilizing a soap film is the well-known "Marangoni effect" [4]. Further, many kinds of soap bubbles are widely used in general applications, including giant, long-lasting, and detergent-only soap bubbles.

In this study, high school students experienced basic thin-film material chemistry by trying to produce a long-lasting spherical bubble on a solid surface. For instance, the student discussed the relationship between the structure of the polymers in the soap bubbles and the bubble longevity. Specifically, the following research question was posed: Does a soap bubble exist that is stable in both hydrophobic air and on a hydrophilic solid surface? This is of interest because a surfactant can be used to decrease the surface tension of a hydrophobic bubble in order to stabilize it in air. However, such a bubble will typically rupture upon impact with the ground (landing).

## 1.1. Learning Objectives

The objective of this experiment is to introduce students to material chemistry through a familiar plaything. As a teaching material, soap bubbles are used because students show interest in the science of toys. The stability, size, and color of soap bubbles depend upon chemistry and physics. Through designing long-lasting soap bubbles and discussing the reasons behind their longevity, students can experience basic material chemistry.

## 2. Pre-lab. Learning

In the pre-lab learning activity, students learned about the chemistry, physics, and mathematics related to soap bubbles.

### 2.1. Learning about Soap Bubble

#### 2.1.1. The Structure of Soap Bubble

A surfactant molecule consists of a hydrophilic head and hydrophobic tail. Typical functional head groups are sulfate, carboxylate, and amino groups. The tails, in contrast, consist of alkyl groups. The heads are soluble in water (hydrophilic), while the tails are insoluble in water (hydrophobic).

Surfactants occur in four structural types (Figure 1):

—cationic surfactant: Often used for antimicrobial purposes, such as benzalkonium chloride. The ammonium ion is the cationic group.

—anionic surfactant: These are the major surfactants in detergents. Sulfate and carboxylate groups are the typical anionic groups.

—zwitterionic surfactant: This type of surfactant is often used in mild detergents for sensitive skin.

—neutral surfactant: This type of surfactant is often used in mild detergents for sensitive skin.

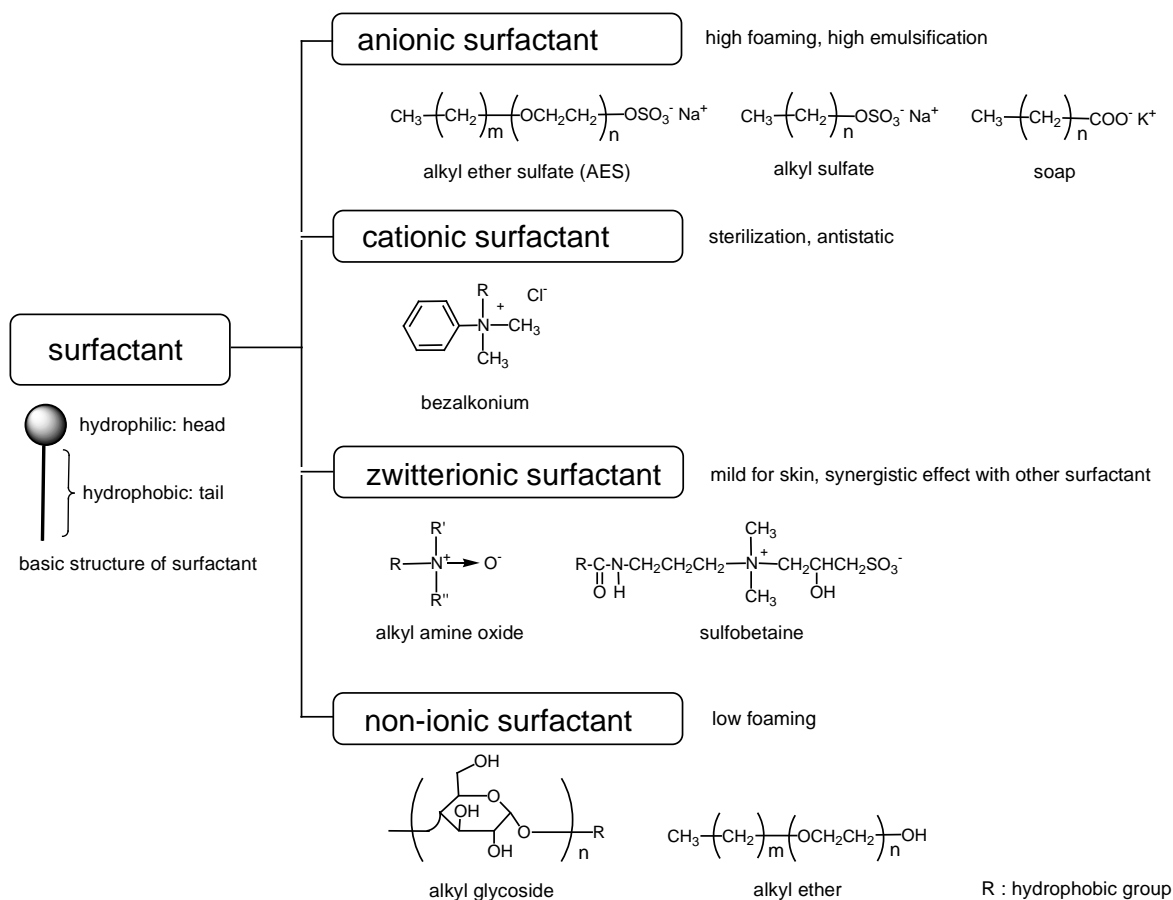


Figure 1. Structure of surfactants

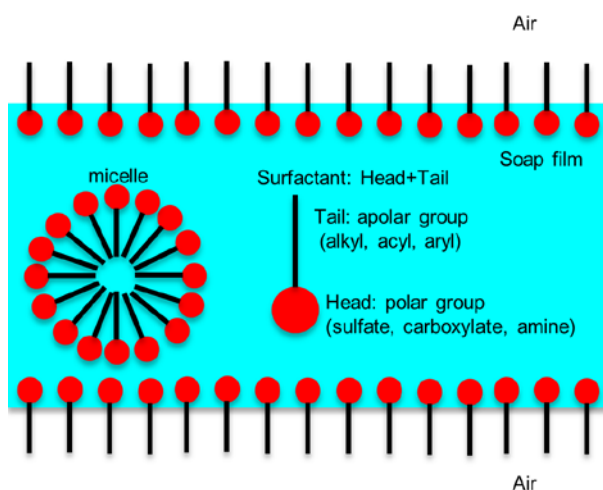


Figure 2. Structure of a soap bubble and a soap film

At the interface between a soap film and air, the surfactant tends to form a monolayer in which the heads are directed toward the aqueous phase and the tails are directed toward the air (Figure 2). Surfactants are adsorbed at the interface between water and air to reduce surface tension. If the concentration is high enough, it will form a micelle. The concentration of the surfactant at

which micelle formation starts is known as the critical micelle concentration (CMC). However, increasing the surfactant concentration beyond the CMC results in a gradual increase in the surface tension (Figure 3).

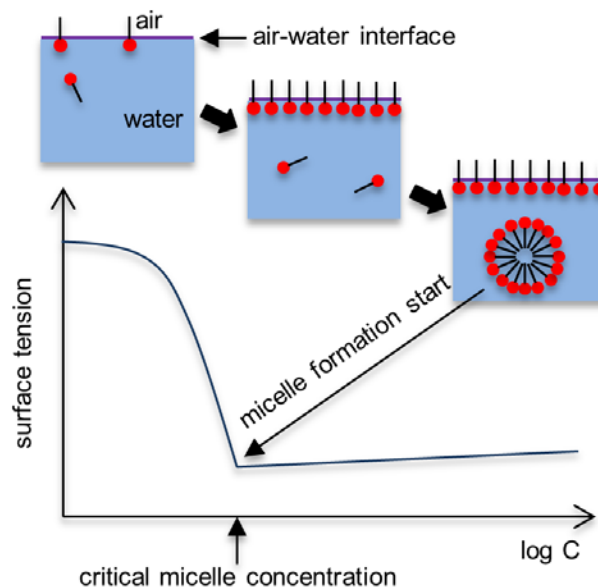


Figure 3. Surface tension and surfactant concentration

The incorporation of polymers in soap bubbles imparts mechanical strength because the polymer solution exhibits viscous and elastic behaviors (Figure 4). Sucrose and glycerol would be expected to strengthen the soap bubble and help to avoid desiccation because those molecules can form hydrogen bonds between water, the polymer, and other components in the soap bubble. In addition, those molecules often act as plasticizers (for example, glycerol is used as an industrial plasticizer for PVA). A plasticizer is an additive that increases the plasticity or fluidity of a material and it is important for toughening materials. Here, the term 'toughening' is not the same as 'hardening.' Often, hard materials are fragile (brittle) against impact. Unbreakable soap bubbles should be tough, because they land on solid surfaces.

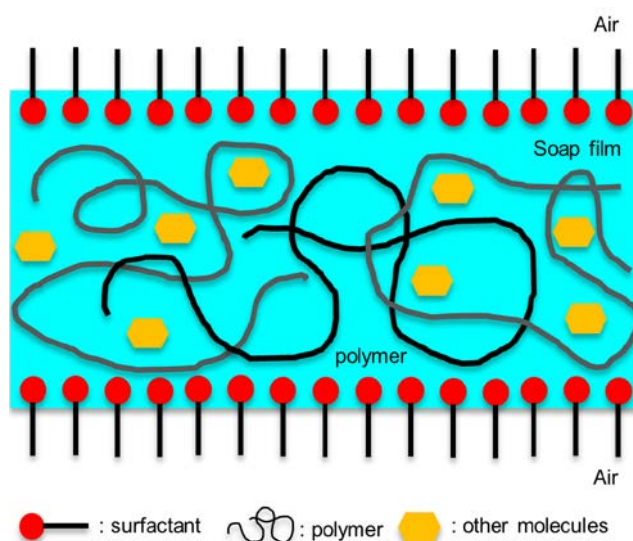


Figure 4. Structure of soap bubble

The polymer increases the mechanical strength of the soap film by the viscoelastic behavior of the polymer solution. Poly(vinyl alcohol) (PVA) is commonly used in soap bubbles. The structures of the polymers used in this experiment are shown in Figure 5.

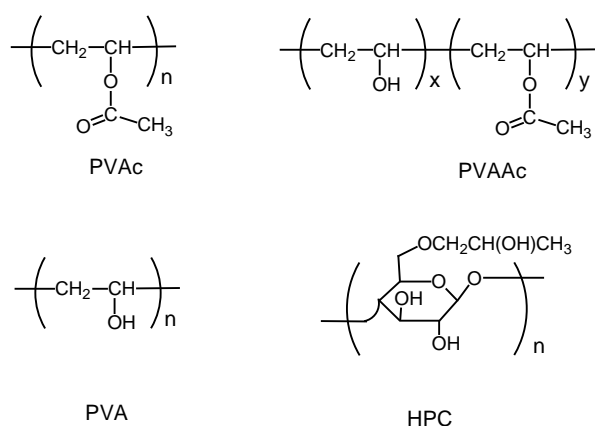


Figure 5. Structure of polymers

PVA is synthesized by the deacetylation of PVAc. Various PVAs having different degrees of deacetylation are commercially available. In this paper, we designated "86–90% deacetylated PVA ("poly(vinyl alcohol)1000, partially hydrolyzed") as "PVAAc." PVAs having different degrees of deacetylation show different physical properties. For example, the viscosity of an aqueous

solution of 100% deacetylated PVA (fully hydrolyzed PVA) gradually increases over time, although PVAAc, in contrast, does not [5]. It is believed that the hydrophobicity of the acetyl groups in PVAAc inhibits the crystallization of PVA.

Hydroxypropyl cellulose (HPC) is water soluble cellulose derivative. HPC is used as a food additive.

PVA forms isolated coils at low concentrations and entangled chains at high concentrations (Figure 6) [6]. This change affects the viscosity and elastic behavior of the PVA solution, which also depends on the molecular weight and degree of deacetylation of the PVA [6].

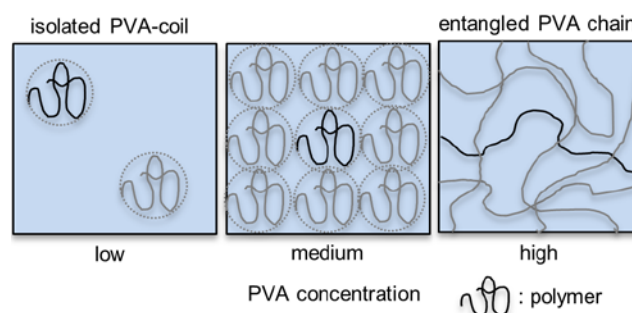


Figure 6. Relationship between polymer concentration and physical behavior

It is well known that the color of a soap bubble changes during flight, which is due to desiccation and the reduction in the film thickness [7,8,9]. However, the bubble colors depend on both the viewing angle and the film thickness.

### 2.1.2. Learning about The Marangoni Effect

Local differences in the composition or temperature of a soap bubble cause local variations in the interfacial tension, which produces movement at the fluid interface. This bulk flow, or Marangoni effect, stabilizes the soap bubble because the surfactant molecules can be restored to the stretched part of the soap bubble film (Figure 7) [10]. This effect stabilizes a bubble film under the influence of a surfactant. The Marangoni effect also decreases the ascension velocity of an air bubble in surfactant-containing water [11].

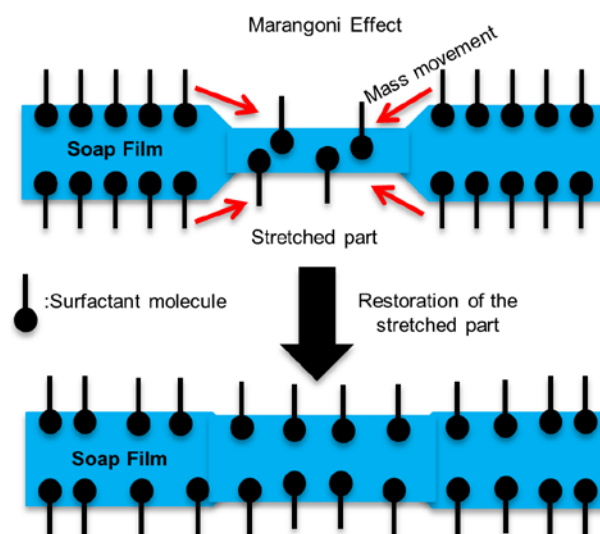


Figure 7. The Marangoni Effect

Students can observe colors moving on the soap bubble surface. This is described as Marangoni flow. Other

examples of the Marangoni effect include the ‘tears’ observed in wine, the spontaneous motion of a camphor particle on water, and the spontaneous motion of the Belousov-Zhabotinsky reaction.

### 2.1.3. Relationship between the Film Thickness of a Bubble and the Pressure Difference—the Laplace-Young Equation

The Laplace-Young equation yields the pressure difference via equation 1 [12].

$$P_i - P_o = 2\gamma / r \quad (1)$$

where  $P_i$  and  $P_o$  are the internal and external pressures of the bubble, respectively,  $\gamma$  is the surface tension, and  $r$  is the bubble radius (Figure 8).

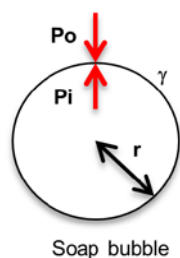


Figure 8. Inside and outside pressure difference in a soap bubble

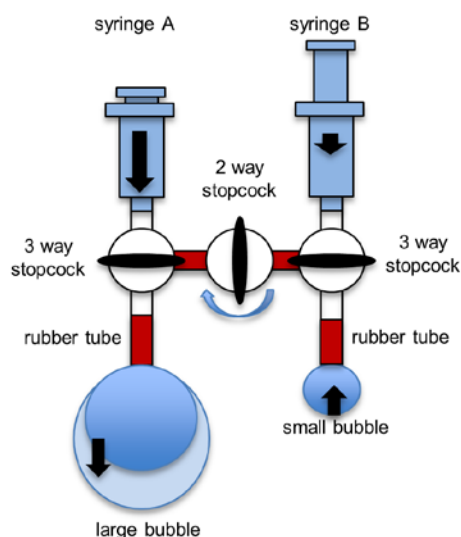


Figure 9. Schematic of the apparatus for the double-bubble demonstration

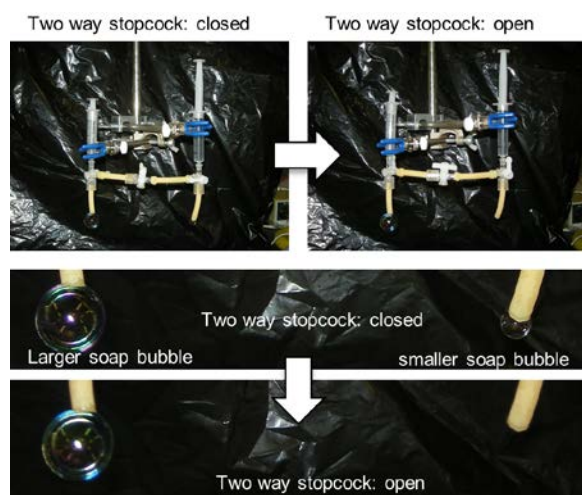


Figure 10. The apparatus for the double-bubble demonstration (pictures)

If two differently sized soap bubbles are connected together, the smaller bubble becomes smaller and larger bubble becomes larger. There are two reasons for this behavior: 1) the pressure difference is decreased by the increasing bubble diameter, and 2) the surface area becomes smaller. The instructor can demonstrate this with the apparatus shown in Figure 9 and Figure 10.

### 2.1.4. Color of Soap Bubbles—the Refraction of Light [13]

Light of different wavelengths has different refractive indexes. Equation 2 shows that the bubble colors (i.e., the wavelength of the refracted light) depend on both the viewing angle and the film thickness. Equation 2 gives the condition for interference, as shown in Figure 11.

$$2nt\cos\theta = (m + 1/2)\lambda \quad (2)$$

where  $t$  is the film thickness—optical path difference,  $\theta$  is the angle of refraction related to the viewing angle,  $\lambda$  is the wavelength of the incident light ray, and  $n$  is the refractive index.

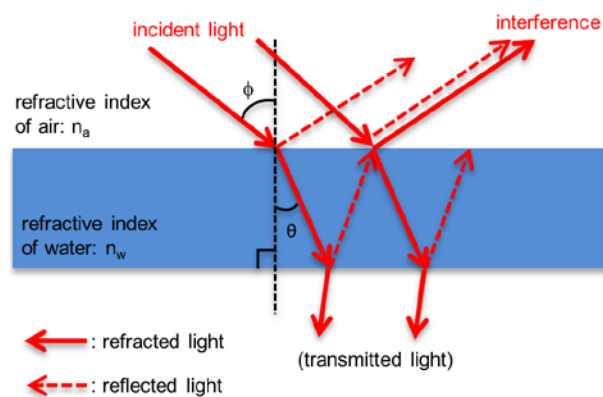


Figure 11. Refraction of light

You can see the coin at the bottom of the cup.

You can't see the coin at the bottom of the cup.

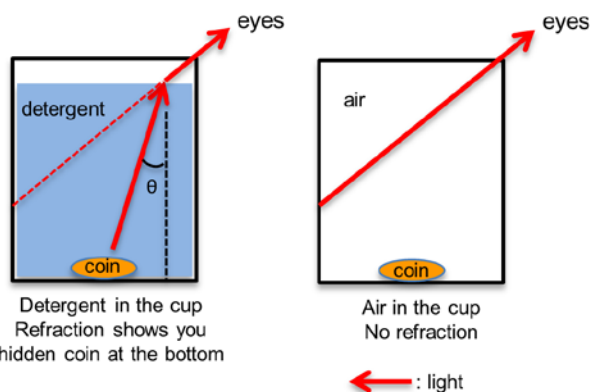
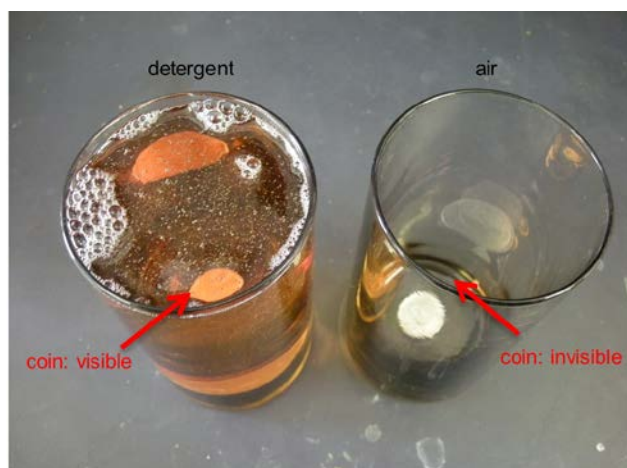


Figure 12. The refraction of light shows the coin at the bottom of a cup

The refraction of light can be observed easily by using detergent in a cup (salad oil is also good for this observation). Various experiments have been reported for learning about refraction. We often use an experiment in which students observe a coin at the bottom of a cup with or without detergent in the cup (Figure 12 and Figure 13). The refractive indexes of the air and detergent are 1.0 and 1.4, respectively. The large difference between the refractive indexes results in a large refraction of the light. Students view both cups at the same angle, and can see the



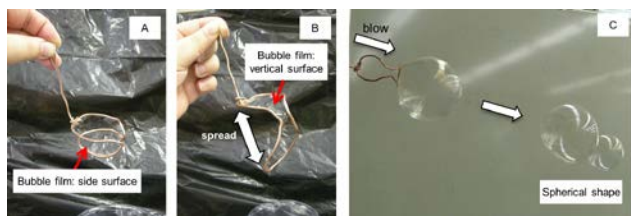
coin at the bottom of the cup with the detergent, but not in the cup without detergent.



**Figure 13.** The refraction of light shows a coin at the bottom of a cup (picture). JOY was used as a detergent

### 2.1.5. Mathematics of Soap Bubbles—Why are Soap Bubbles Spherical?

When you dip a loop of wire into a soap solution, the surface of the film that forms represents the minimum mathematically possible area for the loop. This idea is embodied in Plateau's problem, which endeavors to show the existence of a minimal surface within a given boundary [14]. Plateau experimented with soap films to solve the problem. The instructor can effectively show students a minimal surface with a given boundary by a demonstration with a wire (Figure 14).



**Figure 14.** Minimal surface with a given boundary

As shown in Figure 14, there are two possible saddle-shaped film surfaces. The soap film tends to form figures of *minimum surface* area. When the side surface is smaller than the vertical surface, the soap film forms on the side surface (Figure 14A). When the height of the wire is increased by spreading, the side surface area is increased and the soap film forms on the vertical surface of the wire (Figure 14B). If there is no wire, a soap film adopts the shape of a sphere to minimize its surface area (Figure 14C).

## 2.2. Formulating the Hypothesis

A soap-bubble solution with a high glycerol ratio often yields a long-lasting bubble, because glycerol delays bubble desiccation through the formation of hydrogen bonds, lengthening the bubble lifetime [15]. On the other hand, students hypothesized that the desiccation of the soap bubble may leave a resin film, affording an unbreakable sphere.

Students formulated a hypothesis that partially hydrolyzed poly(vinyl alcohol) (PVAAc) would yield an unbreakable soap bubble, similar to a polyballoon,

because this substance is an intermediate compound between poly(vinyl acetate) (PVAc), which is used for polyballoons and chewing gum bases, and poly(vinyl alcohol) (PVA), which is used for the production of large soap bubbles and laundry starch.

## 3. Materials and Methods

### 3.1. Materials

The ingredients used in this experiment was summarized in Table 1.

### 3.2. Experimental Procedure

#### 3.2.1. Various Soap Bubble

Soap-bubble solutions composed of various kinds of polymers and detergents were prepared and compared. After describing the chemical components of the soap bubbles, the students chose the detergent, polymer, and other chemicals for their experiments. To prepare the soap-bubble solutions, the polymer was first dissolved in deionized water. Glycerol or sucrose was then dissolved in the polymer solution. Finally, the chosen detergent was mixed into the solution carefully to prevent foaming. Soap bubbles were blown by means of a cone-shape blower.

##### 1. Preparation of polymer solution

—PVA solution: Commercially available PVA laundry starch (8% PVA aqueous solution) was used.

—PVAc emulsion: Commercially available PVAc laundry starch was used.

—PVAAc solution: PVAAc is difficult to dissolve in water. PVAAc (50 g) was swelled in deionized water (500 mL) in a 1 L Erlenmeyer flask overnight. The mixture was heated in a hot water bath at 80 °C and often stirred with a stirring rod to afford the PVAAc solution.

—HPC solution: HPC (50 g) was swelled in deionized water (500 mL) in a 1 L Erlenmeyer flask. The mixture was heated in a hot water bath at 80 °C and often stirred with a stirring rod to afford the HPC solution.

##### 2. Preparation of soap solution

—Check the ingredient information on the detergent bottle label to determine the name of the first surfactant listed.

—Transfer the polymer solution (10 mL) into a 50 mL glass bottle with a 10 mL pipette.

—Dissolve sucrose or glycerol in the polymer solution. Stir the mixture carefully with the cone-shape blower.

—Add the detergent carefully into the mixture to avoid forming bubbles. Stir the mixture carefully with the cone-shape blower.

##### 3. Blowing soap bubbles

A group of 3 students is ideal for this experiment.

—Student A blows the soap bubble with the cone-shape blower. Producing 10 to 30 soap bubbles with ~3 cm diameters at once is preferred.

—Student B counts the number of bubbles produced in one blowing.

—Student C counts the unbreakable bubbles from one blowing and records the data.

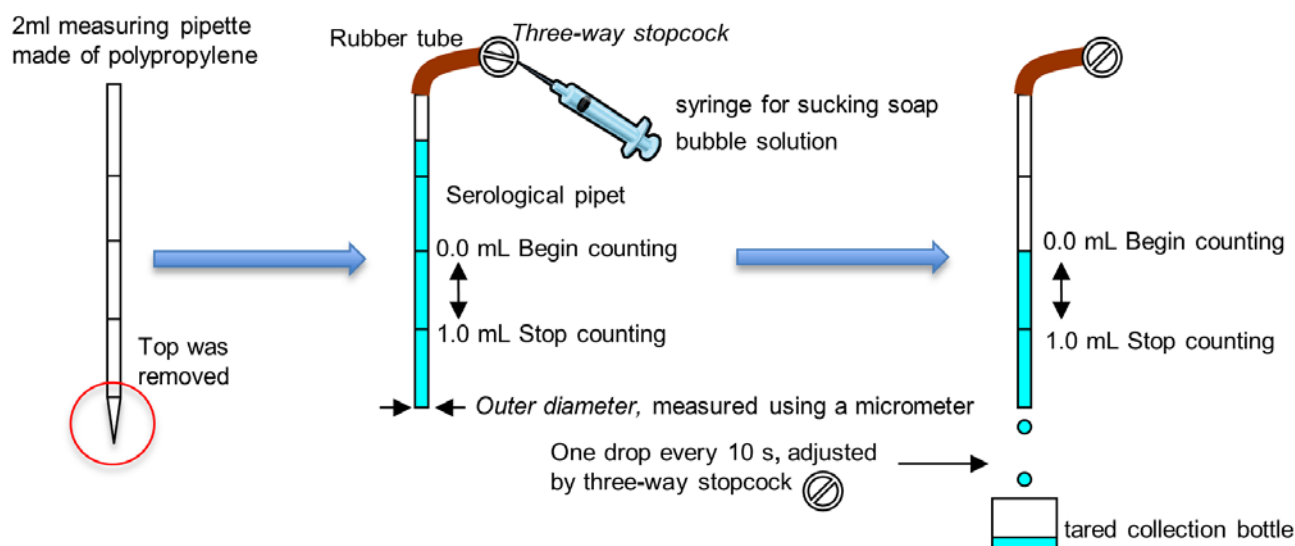
—The number of unbreakable bubbles is calculated as an average of five replicate experiments.

The best place for the long-lasting bubble experiment is outdoors, because low humidity, high temperature, and breezy conditions are preferable for the desiccation of the soap bubbles. A courtyard is more amenable for counting the number of unbreakable bubbles, because it is difficult to count the bubbles as they float away in a more open space (e.g., public park).

Note: The ground, especially if surfaced with concrete or tiles, is made slippery by the soap bubbles used in these experiments. Furthermore, if the surface is washed, it becomes increasingly slippery until the soap has been completely washed away. The resin that remains on the ground can be washed away with water after the soap bubble experiments have been concluded.

**Table 1. Material data and suppliers**

Product	Molecular Formula	Supplier	CAS registry number
PVA laundry starch	$\left( \text{CH}_2 - \underset{\text{OH}}{\text{CH}} \right)_n$ (8% aqueous solution of poly(vinyl alcohol))	Rocket Soap	9002-89-5
Laundry starch consisting of PVAc dispersion	$\left( \text{CH}_2 - \underset{\text{O}-\text{C}(=\text{O})-\text{CH}_3}{\text{CH}} \right)_n$ (main chemical composition: poly(vinyl acetate))	Kao	9003-20-7
Polyvinyl alcohol partially hydrolyzed (PVAAc) (saponification degree: 86.0–90.0 mol%)	$\left( \text{CH}_2 - \underset{\text{OH}}{\text{CH}} \right)_x \left( \text{CH}_2 - \underset{\text{O}-\text{C}(=\text{O})-\text{CH}_3}{\text{CH}} \right)_y$	Wako Pure Chemical Industries, Ltd.	9002-89-5
Hydroxypropyl cellulose (HPC) (2.0-2.9 cP)	$\left( \text{C}_6\text{H}_7\text{O}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3 \right)_n$	Wako Pure Chemical Industries, Ltd.	9004-64-2
“CHARMY Foam Power”	$\text{R}-\left( \text{OCH}_2\text{CH}_2 \right)_n-\text{OSO}_3^- \text{Na}^+$ (main surfactant: sodium alkyl ether sulfate)	LION	Japan Article Number: 4903301093435
“Cucut Hand Beauty”	$\left( \text{C}_6\text{H}_7\text{O}_2\text{OR} \right)_n$ (main surfactant: alkyl glycoside)	Kao	Japan Article Number: 4901301264077
“CHARMY Magicka”	$\text{R}-\text{N}^+(\text{R}')_2-\text{O}^-$ (main surfactant: alkylamine oxide)	LION	Japan Article Number: 4903301189848
“JOY”	$\text{R}-\left( \text{OCH}_2\text{CH}_2 \right)_n-\text{OSO}_3^- \text{Na}^+$ (main surfactant: sodium alkyl ether sulfate)	P&G	Japan Article Number: 4902430982221
“Cucut clear sterilization”	$\text{CH}_3-\left( \text{CH}_2 \right)_n-\text{OSO}_3^- \text{Na}^+$ (main surfactant: alkyl sulfate)	Kao	Japan Article Number: 4901301288561
Glycerol	$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	Wako Pure Chemical Industries, Ltd.	56-81-5
Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	Wako Pure Chemical Industries, Ltd.	57-50-1



**Figure 15.** Schematic of surface tension measurement apparatus

### 3.2.2. Surface Tension Measurement

To determine the relationship between the lifetime and the surface tension  $\gamma$  of a soap bubble, the  $\gamma$  values of the soap solutions were measured. The surface tension was measured using the drop-weight technique, which did not require the use of a stalagmometer (Figure 15, Figure 16). The number of drops from 1 mL of the soap-bubble solution was counted and collected, and the average mass per droplet was calculated for each solution. The surface tension  $\gamma$  was then calculated according to equation 3.

$$\gamma = \Phi Mg / 2\pi r \quad (3)$$

Where  $M$  is the weight of one droplet,  $g$  is the gravitational acceleration, and  $2\pi r$  is the circumference ( $r$ : radius) of the measuring pipette.

$\Phi$  is the Harkins-Brown correction factor [16]. The Harkins-Brown correction factor in the literature was plotted with Microsoft Excel and the factor  $\Phi$  was approximately represented by equation 4:

$$\Phi = -4.91x^6 + 24.2x^5 - 44.6x^4 + 37.9x^3 - 15.7x^2 + 3.63x + 0.999 \quad (4)$$

where  $\Phi$  is the correction factor and  $x$  is  $r/V^{1/3}$ .

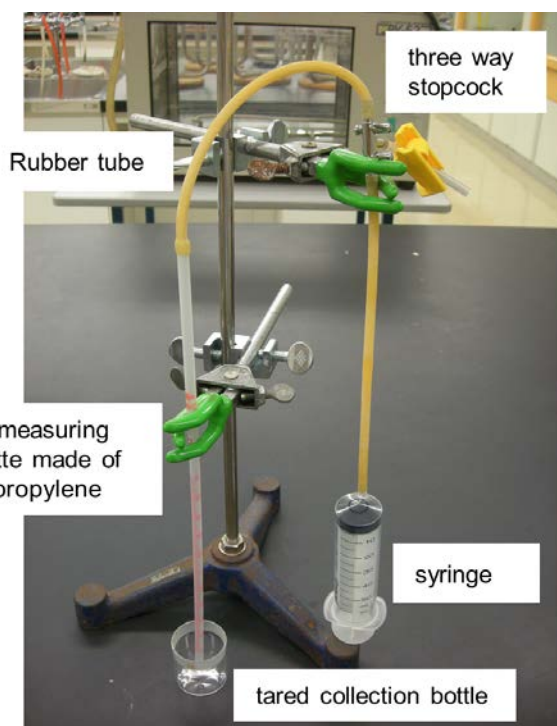


Figure 16. Surface tension measurement apparatus (picture)

Table 2. Sample surface tension data obtained for the bubble solutions

No.	$r \times 10^{-3}$ (m)	Density ( $\text{kg/m}^3$ )	Number of droplets (1 mL)	Dropped solution weight $\times 10^{-3}$ (kg)	Weight of one droplet $M \times 10^{-6}$ (kg)	Volume of one droplet $V \times 10^{-9}$ ( $\text{m}^3$ )	$r/V^{1/3}$	Correlation Factor <sup>a</sup>	Surface tension (mN/m)
1	3.13	1050	32	0.994	31.1	29.6	1.01	1.51	23.4
2	3.13	1010	24	0.885	36.9	36.5	0.943	1.57	28.8
3	3.13	1010	29	1.01	34.7	34.3	0.963	1.55	26.9
4	3.13	1090	30	0.906	30.2	27.7	1.03	1.49	22.4
5	3.13	1070	31	0.960	31.0	29.0	1.02	1.50	23.2
6	3.13	1130	34	1.24	36.6	32.4	0.982	1.54	28.0

<sup>a</sup>The Harkins-Brown correction factor was calculated by following equation:

$$\Phi = -4.91x^6 + 24.2x^5 - 44.6x^4 + 37.9x^3 - 15.7x^2 + 3.63x + 0.999$$

where  $\Phi$  is the correction factor and  $x$  is  $r/V^{1/3}$ .

A disposable measuring pipette was used for droplet counting; this device is quite inexpensive and the samples are too viscous for a capillary-type stalagmometer to be used. The bottom of the measuring pipette was filed flat and the collection bottle was weighed before the experiment. The soap-bubble solution was pumped into the Measuring pipette via suction by a syringe, the stopcock was closed, and the syringe was removed. The dropping speed was adjusted to approximately 1 droplet every 10 s, by varying the angle of the three-way stopcock. The droplets were counted and collected inside the tared collection bottle, which was then weighed. The average data are summarized in Table 2. By this simplified method, the surface tension of deionized water was 67.9 mN/m, whereas the exact surface tension of water at 20 °C is 72.8 mN/m [17]. However, this simplified method is sufficient for comparing the surface tensions of various soap bubble solutions in this laboratory experiment. This simplified method requires no specialized equipment and the procedure is easily performed.

### 3.2.3. Relationship between the Humidity and Lifetime of Soap Film

To determine the relationship between the relative humidity (RH) and lifetimes of the soap bubbles, the

longevities of soap films were measured at four RH levels. To prepare a film from solution No. 1, a plastic cup (diameter, 56 mm; height, 68 mm) was dipped into soap solution No.1 in a laboratory dish (Figure 17). A soap film formed on the rim of the cup. The cup was stored in a glove box. The RH was adjusted by storing the drying agents calcium chloride and silica gel inside the glove box. Three cups were examined at the same time for one humidity condition to obtain an average lifetime.

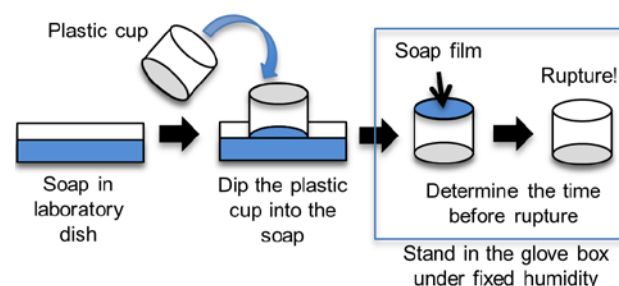


Figure 17. Relationship between humidity and soap film lifetime

The experimental setup used in the glove box is shown in Figure 18. The humidity inside the glove box can be decreased with calcium chloride. If the laboratory is dry, the humidity of the room should be kept high by using a



humidifier for the experiment at high humidity. Because the humidity inside the glove box gradually decreases, this experiment requires 2 days. If the instructor uses a desiccator instead of a glove box, the experiment can be completed in 1 day.



Figure 18. Appearance of the glove box



Figure 19. Use of desiccators in lieu of a glove box

A glove box is not essential for this experiment, because a desiccator can be used in its place (Figure 19). A desiccator with a silica-gel desiccant provides a low humidity environment, whereas higher humidity can be obtained without the silica gel. Students can compare the lifetimes of soap films at two humidity levels.

### 3.3. Hazards

PVA, sodium sulfate, and PVAAc are neither hazardous nor classified as dangerous. PVAc may cause irritation to the eyes, skin, digestive tract, and respiratory tract. The surfactant included in the detergents may cause eye damage. HPC is unlikely to cause eye or skin irritation, or other injury.

## 4. Results and Discussion

### 4.1. Various Soap Bubble

As shown in Table 3, six characteristic soap bubbles were prepared using the various polymer and detergent solutions, which were then compared. Photographs of the obtained soap bubbles are presented in Figure 20. Bubble-type No. 1 in Table 3 (hereafter referred to as simply “No. 1”) is a soap bubble that often retained its spherical shape on a solid surface for several hours to as long as one day, depending on the weather. Eventually, No. 1 either ruptured or retracted, leaving a disc-shaped resin film on the surface. No. 2 yielded a giant bubble, while No. 3 exhibited aerial flight times of over 1 min. The only difference between No. 1 and No. 3 was the low-molecular-weight component, i.e., sucrose or glycerol; however, No. 3 was ruptured by landing. As shown in Figure 20, the soap bubbles of type No. 4 often appeared to consist of a lower hemisphere only, because cloudiness accumulated in that region. No. 5 constituted the most unstable bubble type, which often appeared to vanish when ruptured. Finally, bubble-type No. 6 shown in Table 1 was a long-lasting hemispherical bubble when grounded on an indoor desk; however, this bubble type was quite vulnerable to wind.

Table 3. Soap Bubble Properties

No.	Polymer added	Detergent added (main surfactant) <sup>b</sup>	Other additives	Properties	Surface tension (mN/m)
1	9w/w% PVAAc 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	Long-lasting on solid surfaces as spherical bubbles	23.4
2	PVA laundry starch <sup>a</sup> 10 mL	CHARMY Foam Power (AES) 1 mL	Glycerol 1 mL	Giant	28.8
3	9w/w % PVAAc 10 mL	CHARMY Foam Power (AES) 1 mL	Glycerol 1 mL	Long flight time in air	26.9
4	9w/w % PVAAc 10 mL	Cucut Hand Beauty (AG) 1 mL	-	Often the upper hemisphere seems to be absent	22.4
5	9w/w % HPC 10 mL	Cucut Hand Beauty (AG) 1 mL	Sucrose 1 g	Unstable in air and on solid surface	23.2
6	1/4-diluted PVA laundry starch 2 mL	1/8-diluted “CHARMY Foam Power” (AES) 2 mL	Glycerol 8 mL	Long-lasting on solid surfaces, hemispherical bubbles	28.0

<sup>a</sup> PVA laundry starch consisting of 8 w/w% PVA.; <sup>b</sup> AES: alkylether sulfate; AAO: alkylamine oxide; AS: alkyl sulfate





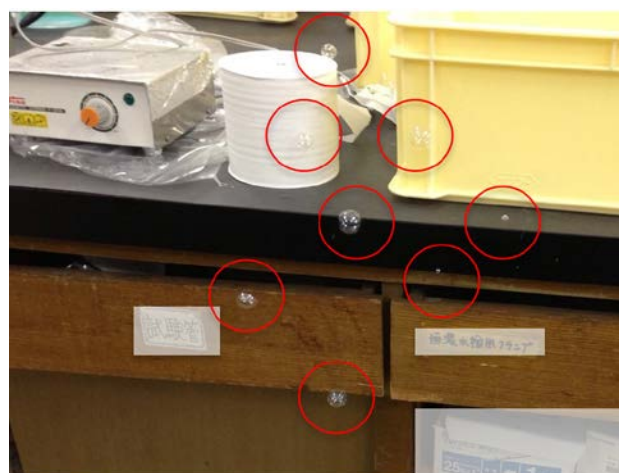
**Figure 20.** Six kinds of soap bubbles. 1) No. 1: Spherical bubble attached to the building wall; 2) No. 2: Giant soap bubble; 3) No. 3 on the concrete. This bubble floated in the air for over 1 min and was often long-lasting on the ground; 4) No. 4: Often the upper hemisphere seemed to be absent; 5) No. 5: Unstable in air and on a solid surface; 6) No. 6: a long-lasting hemispherical bubble on a solid surface

Soap bubble No. 1 was often long lasting on a solid surface, with its stability depending on the ambient conditions, i.e., the temperature, humidity, wind, etc. These soap bubbles were examined both outdoors and indoors. Outdoors, No. 1 was stable on both grass and a wooden deck (Figure 21). Inside the laboratory, the soap bubbles were stable on toilet paper, a plastic container, a laboratory bench, and a wooden cabinet (Figure 22). The No. 1 soap bubble ruptured in the following three ways: explosion in the air or on a solid surface; deflation on a solid surface over a few minutes or hours; or deflation in air followed by the descent of the resin to the ground.

Students learned that the features of the soap bubbles drastically change depending on their chemical composition.



**Figure 21.** No. 1 soap bubbles outdoors. The soap bubbles were stable on grass and a wooden deck



**Figure 22.** No. 1 soap bubbles in the laboratory. The soap bubbles circled in red were stable on toilet paper, a plastic container, a laboratory bench, and a wooden cabinet

## 4.2. Surface Tension

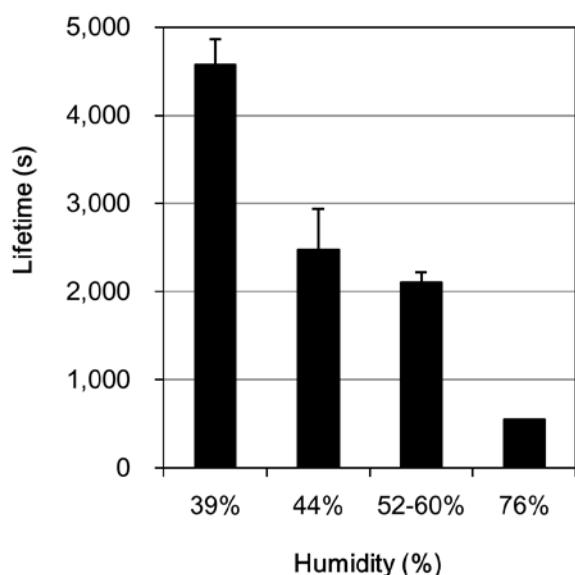
Surface tension is an important parameter that affects the stability of a soap bubble in air, because the pressure difference between the interior and exterior of the bubble depends on both the surface tension and the bubble radius. The Laplace-Young equation yields the pressure difference (equation 1). [18]

If the  $\gamma$  value of the soap bubble is reduced, the pressure difference between the interior and exterior of the bubble is decreased. For example, the surface tension of water at 20 °C is 72.8 mN/m [19], whereas that of soap bubble No. 1 (Table 2) at 20 °C is 23.4 mN/m. For a bubble diameter of 0.01 m, the pressure differences are calculated as 7.28 Pa for water and 2.34 Pa for soap bubble No. 1.

Bubble-type No. 2, which is a giant soap bubble, possesses the highest surface tension of the six kinds of soap bubbles (Table 2). No. 1, which is often stable on a solid surface, e.g. grass, concrete, tile, and the ground, exhibits a low surface tension. Although the surface tension may be affected by the viscosity of the soap-bubble solution, all of the bubble types, which had varying solutions, exhibited similar surface tensions. These results suggest that the stability of a soap bubble in air or on a solid surface depends not only on the surface tension, both also on other factors, e.g., the mechanical strength provided by the polymer component.

## 4.3. Relationship between the Humidity and Lifetime of Soap Film

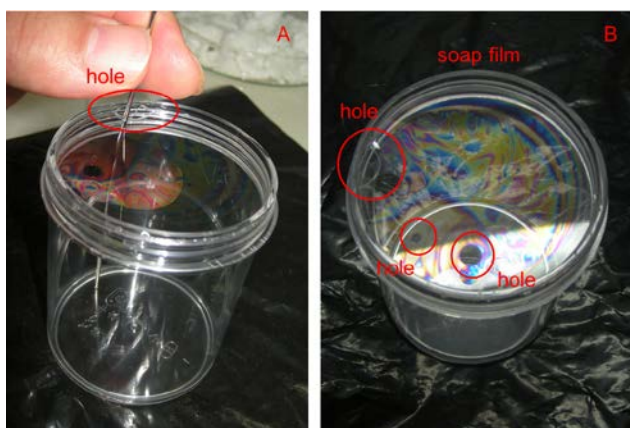
From the results of the surface tension experiments, the students hypothesized that the low surface tension of film No. 1 was not the singular reason for its long lifetime. The lifetime of the film tended to be prolonged with decreasing humidity (Figure 23). In terms of lifetime endpoints, the soap films at relative humidity (RH) levels of 40% and 44% tended to shrink around the rims of the cups, whereas those at 52–60% and 76% RH levels ruptured. At 40% RH, soap film No. 1 produced a film with holey defects which was not broken by soft poking with a wire. After desiccation, soap film No. 1 became more stable than when freshly prepared.



**Figure 23.** Relationship between the humidity and the lifetime of soap film No. 1 at 24 °C

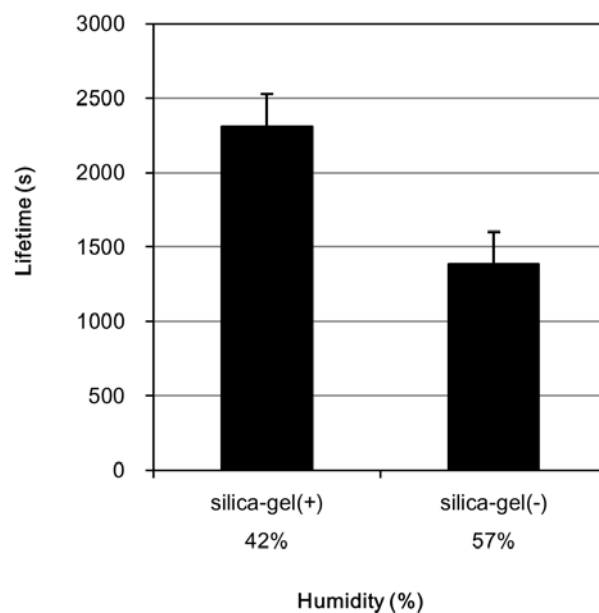
The lifetime of the soap film in the desiccator tended to be shorter than that in the dry glove box, because the humidity gradually decreases in the desiccator. A hygrometer showed that the humidity in the desiccator with silica gel was 61% at 0 min (the time that the film was introduced), but gradually decreased to 42% at 20 min.

To examine the number of unbreakable soap films that formed on the rims of the plastic cups, 10 soap films were stored at two humidity levels in the glove box (39% and 65%). After 24 h, the number of remaining films was counted. Two films remained at 39% RH, and zero films remained at 65% RH. One film did not rupture at all, even after more than two month in the glove box. The film also did not rupture after pricking to form a hole (Figure 24). It is notable that the PVA soap solution (PVA laundry starch : sucrose : detergent 1 = 10 mL:1 g:1 mL) also produced a dried film on the rim of the cup in the glove box.



**Figure 24.** (A) A wire was inserted into the soap film, producing a hole. (B) Holes in the film after 4 h

As shown in Figure 25 the lifetime of the soap film in the dry desiccator is longer than that in the non-dried desiccator. The experiment can be carried out in one 50 minute class period.



**Figure 25.** Relationship between the humidity and lifetime of soap film No. 1

#### 4.4. Relationship between the Humidity and Lifetime of Soap Bubble

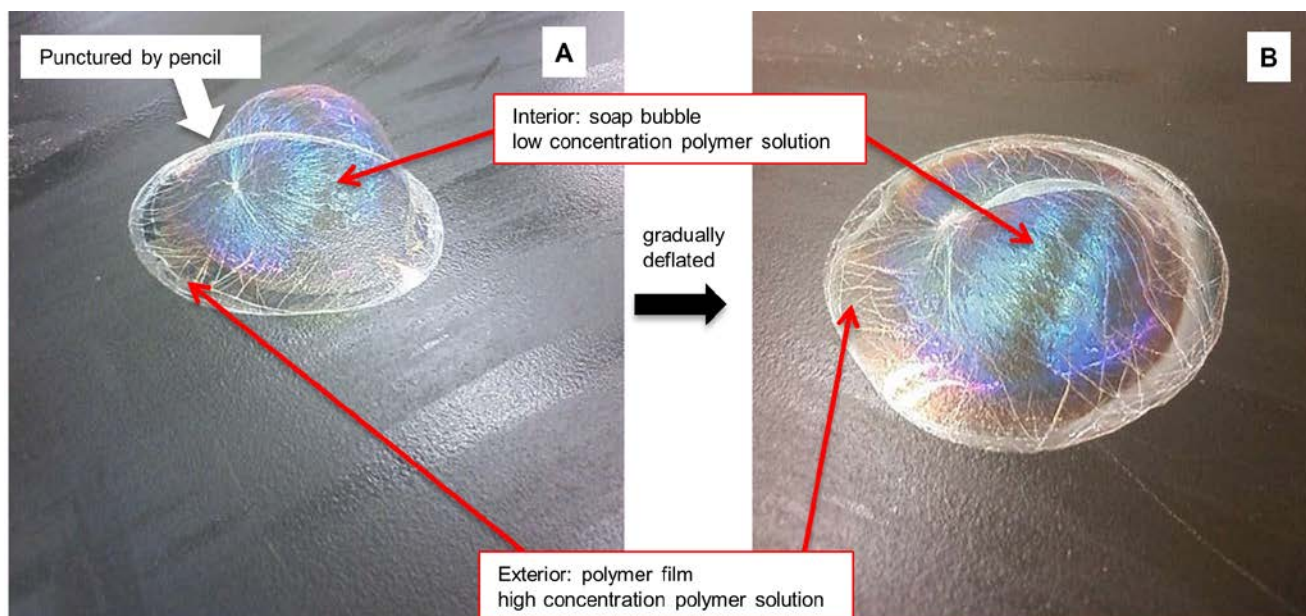
To form a stable No. 1 bubble on a solid surface, over 15-s flight time is required before contact with the ground. It is notable that the students found that No.1 had the greatest stability on a solid surface in an air-conditioned laboratory in winter (typical room temperature: 22 °C; RH: 40%; weak air current from an air conditioner) and outdoors in summer (typical outdoor temperature range: 22.6–31.3 °C; RH: 56%; weak wind). Note that both conditions promote bubble desiccation.

To examine its structure, No. 1 was blown in the air and allowed to become grounded on a laboratory bench, where it retained its spherical shape. The bubble was then punctured with a sharp pencil, whereupon it was seen that the ruptured bubble consisted of two phases (Figure 26): an internal soap bubble and an external resin film. It was suggested that flight in the air for over 15 s resulted in desiccation of the soap bubble, leading to the formation of an external resin film. This film then behaved as a protective layer for the internal soap bubble. Furthermore, the high concentration of the soap bubble may result in the phase separation of the PVAAc solution, yielding two individual PVAAc solutions, i.e., a dilute and a concentrated viscous PVAAc solution (Figure 27.B-2). Normally, the evaporation of the water in a bubble decreases the film thickness and leads to rupture. The fact that a 15-s flight time before contact with the ground was required to obtain a stable soap bubble may be an indication of the necessary soap-bubble desiccation time for stability. Desiccation of the solvent decreases the solubility of the polymer, at which point phase separation can take place. Phase separation of polymer yields two phases: a high concentration and a low concentration polymer solution. The highly concentrated polymer solution can solidify to form a film after phase separation.<sup>[20]</sup> Moreover, the PVA forms a physically



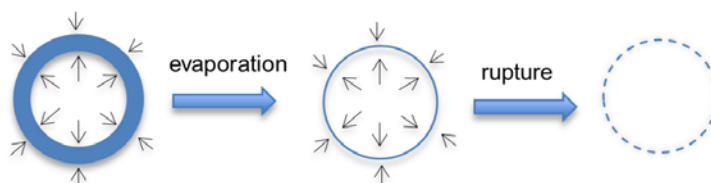
cross-linked gel from an aqueous solution, as reported for the “cast-drying method” [21] or “freezing/thawing technique” [22]. At least, it is possible that desiccation of the bubble solution, i.e., the concentration of the polymer

solution, results in the phase separation of the soap bubble to give a highly concentrated polymer solution (polymer film) and low-concentration polymer solution (soap bubble) (Figure 27.B-2).

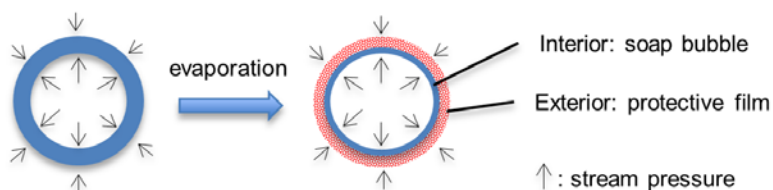


**Figure 26.** Soap bubble on a laboratory bench. (A) The spherical soap bubble, after landing on the laboratory bench, was punctured with a pencil, and exhibited two phases: an external resin film and an internal soap bubble. (B) The punctured bubble gradually deflated to leave a disc-shaped resin film on the laboratory bench

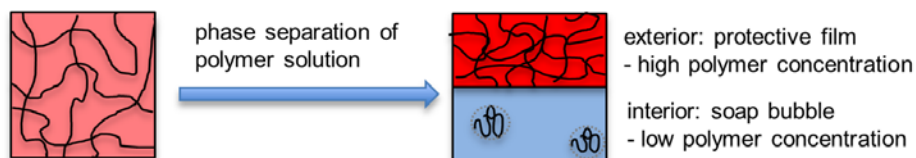
(A) Soap bubble No.2 - 5



(B-1) Soap bubble No.1



(B-2) Phase Separation of No.1 (polymer solution)



**Figure 27.** Proposed bubble structure and rupture mechanism. (A) Nos. 2–5 rupture. (B-1) No. 1 forms a protective film by phase separation of the polymer solution. (B-2) Desiccation of the polymer solution leads to phase separation

The proposed mechanism underlying the formation of long-lasting bubbles through phase separation is supported by the fact that Nos. 1 and 3 exhibited different behaviors, although the difference between these two bubble types was only the low-molecular-weight component, i.e., sucrose or glycerol, as previously stated. Glycerol delays

evaporation from the No. 3 bubbles by forming hydrogen bonds that prevent resin film formation outside of the bubble. Even if No. 3 is evaporated, this bubble still retains its liquid state, because glycerol is liquid at room temperature. On the other hand, sucrose does not prevent the formation of the resin film outside the bubble, because

sucrose is a solid at room temperature. Thus, the evaporation of No. 1 can yield a solid residue.

#### 4.5. Relationship between the Detergent and Lifetime of Soap Bubble

**Table 4. Examples of Unbreakability Properties**

	Polymer added	Detergent added (main surfactant) <sup>a</sup>	Other additive	Unbreakable (%) <sup>b</sup> 28 °C, 70% humidity	Unbreakable (%) <sup>b</sup> 27 °C, 33% humidity
1	PVAAc <sup>c</sup> 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	0	43.0
2	PVAAc <sup>c</sup> 10 mL	JOY (AES) 1 mL	Sucrose 1 g	0	35.1
3	PVAAc <sup>c</sup> 10 mL	CHARMY Magicka (AAO) 1 mL	Sucrose 1 g	0	0
4	PVAAc <sup>c</sup> 10 mL	Cucut clear sterilization (AS) 1 mL	Sucrose 1 g	0	1.4
5	PVA <sup>d</sup> 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	0	35.5
6	PVAc <sup>e</sup> 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	0	0
7	HPC <sup>f</sup> 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	0	0
8	Water 10 mL	CHARMY Foam Power (AES) 1 mL	Sucrose 1 g	0	0

<sup>a</sup> AES: alkylether sulfate; AAO: alkylamine oxide; AS: alkyl sulfate. <sup>b</sup>Bubbles retaining spherical shapes on the ground for more than 10 min were counted as unbreakable. <sup>c</sup>9 w/w% PVAAc was used, <sup>d</sup>Commercial PVA laundry starch (8% PVA) was used, <sup>e</sup>Commercial laundry starch consisting of PVAc dispersion was used, <sup>f</sup>9.1 w/w% HPC in deionized water.

In addition to “CHARMY Soap Power”, other effective detergents for long-lasting bubbles are available. The following detergents were also examined for long-lasting bubbles: JOY (P & G, JAN: 4902430560801), CHARMY Magicka (LION, JAN: 4903301189848), and Cucut *Clear Sterilization* (KAO, JAN: 4901301288561).

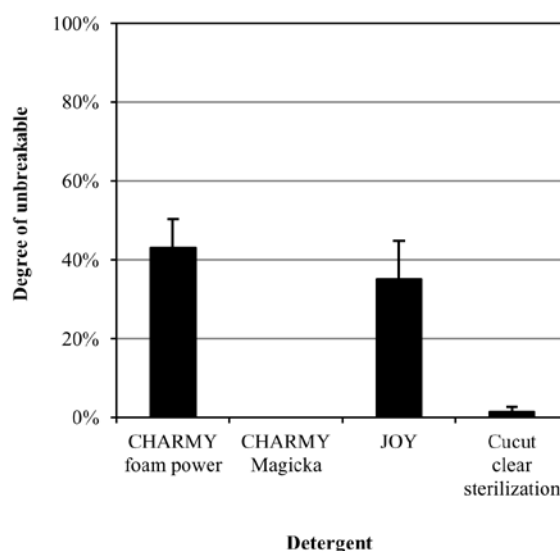
As shown in Table 4 and Figure 28, JOY produced unbreakable bubbles on solid surfaces (concrete, tile, cobwebs, and grass). JOY consists of a AES as the main surfactant, similarly to “CHARMY Soap Power”. The instructor can choose from among a few kinds of detergents that are based on different main surfactants at the stores. Detergents are also available online; one website, as an example, is the Rakuten Global Market. Commercially available detergents often include antifoaming agents, e.g., silicone, fatty acid salts, and polyethers, to control the amount of foam; these components may not be preferable when trying to blow long-lasting bubbles.

As our best condition, PVAAc soap bubble gave 43% of unbreakable bubble on the ground at 27°C, 33% humidity. At that time, PVA soap bubble also gave unbreakable bubble (Table 4).

The lasting time depends on the weather. Degree of unbreakable on ground at representative two conditions were summarized in Table 4. So far as this additional experiment, we counted the bubble kept spherical shape on the ground more than 10 seconds as an unbreakable bubble. Degree of unbreakable of No.1 at 27 °C, 33% humidity (15 July 2015, sunny day) gives 43%, although, degree of unbreakable of No.1 at 28 °C, 70% humidity (27 July 2015, sunny day, next day of taihoon) gives 0%. It is notable that No.5 (PVA: Detergent 1: sucrose = 10ml: 1ml: 1g) gives unbreakable bubble at 27 °C, 33%

humidity. No.5 soap bubble desiccated to give stable spherical bubble on various solid surface.

Students concluded that the soap bubble consists of PVA (PVAAc), AES-detergent and sucrose gives long lasting spherical bubble stable on various solid surface. They showed that low surface tension of the long lasting bubble is not the singular reason for long lasting time.



**Figure 28.** Percentage of unbreakable bubbles depending on detergent at 27°C, 33% RH. PVAAc : detergent : sucrose = 10 ml : 1 ml : 1 g.

## 5. Conclusion

Soap bubbles are good teaching aids for high school chemistry because they are easy to prepare and encompass



many scientific principles and problems. In this experiment, students designed a long-lasting bubble and discussed the mechanism that caused the soap bubbles containing PVA or PVAAc to become stable on a solid surface. It was proposed that bubble flight with a long air time resulted in the external desiccation of the bubble, leading to the formation of an external resin film. This film then behaves as a protective shell for an internal soap bubble. High-school students exhibited the results of this study at the science event, “Sekaiichi Ikitai Kagakuhiroba,” at Iizuka (“The Most Useful Science Plaza in the World,” Iizuka) in 2013 and 2015. During this event, over 500 people participated in soap bubble experiments, i.e., preparing the solutions and blowing soap bubbles. Soap bubbles remain a research subject of ongoing study, engaging not only hobbyists, but also scientists in various fields [23].

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