CHAPTER 2

EXPERIMENTAL SECTION

2.1 Apparatus and components

1. 8-port selection valve (Valco Instruments, www.vici.com)
2. Conductometers (712, Metrohm, Switzerland, www.metrohm.com, and CDM III, Dionex Corp., www.dionex.com)
3. Current-voltage converter (Model 480 picoammeter, Keithley Instruments, www.keithley.com, USA)
4. Data acquisition card (16 bit, PC-Card-DAS16/16AO, Measurement Computing Corp., www.measurementcomputing.com)
5. Diode array spectrophotometer (model 8451, Agilent, www.agilent.com)
6. Gas chromatograph (Model 5890 series II with flame ionization detector (FID), Hewlett Packard, www.gmi-inc.com)
7. Gas chromatograph column (CycloSil-B, Agilent, www.agilent.com)
8. Glass midget bubbler (type 7532, Ace Glass, www.aceglass.com)
9. Ion chromatograph (model DX-100, Dionex, www.dionex.com)
10. Laser source (model LDCU, 3 mW at 409 nm, Power Technology Inc., www.powertechnology.com)
11. Mass flow controller (Model UFC 1000, 0-2 L, www.unit.com and , Model MQV0002B/C, Yamatake, Japan)
12. Operational amplifier (TL082CP, Texas Instruments, www.ti.com)

13. porous polypropylene membrane tube (60 cm x 5.5 mm i.d., Accurel, V8/2, mean pore size 0.2 μm, Membrana Inc., www.membrana.com)
14. Photodiode (BPW34, Siemens, www.siemens.com)
15. Rotameter (Model 1355 Sho-Rate™, Brooks®, www.emersonprocess.com)
16. Solenoid pump, (Model 090SP, Biochem Valve Corp., www.biochemvalve.com)
17. Solenoid valve for gas (Skinner, Skinner valve, www.Parkerhannifin.com)
18. Solid phase micro extraction (SPME) (Polydimethylsiloxane (PDMS) 100 μm, Supelco, www.sigmaaldrich.com)
19. Syringe pump (Model XP3000 with 1000 μL glass barrel syringe, Cavro, www.globalfia.com and model 54022 V6 pump with 19323 8-way distribution valve, Kloehn Ltd., www.kloehn.com)
20. Temperature controller (model TTM-J4 with thermocouple type K, model JW 103-1, Toho, www.toho-inc.co.jp)
21. Vacuum pump (Gast, Model DOA-P104-BN, www.gast.com)

2.2 Chemicals and reagents

All chemicals were of analytical reagent grade except when specified.

1. Alpha cyclodextrin, $C_{36}H_{60}O_{30}$, purum, > 98.0% (Fluka, Germany)
2. Alpha (+) pinene, $C_{10}H_{16}$, purum, > 97.0 % (Fluka, Germany)
3. Alpha(-) pinene, $C_{10}H_{16}$, puriss, > 99.0%. (Fluka, Germany)
4. Glycerol, $C_3H_5(OH)_3$, (Univar, Ajax Finechem, Australia)
5. Hydrogen peroxide, H_2O_2 30% (v/v) (Merck, Germany)
6. Mixed-bed ion exchange resin (Dowex MR-3, DOW, USA)

7. Potassium iodide, KI (Fluka, Germany)
8. Potassium hydrogen phthalate, $KC_8H_5O_4$, , (Fluka, Germany)
9. Sodium hydrogen sulfite, $NaHSO_3$, purum (38-40%) (Fluka, Germany)
10. Sulfuric acid, H_2SO_4 , 98% (w/v) (Merck, Germany)
11. Triton X-100, $C_{14}H_{22}O$, Laboratory grade $(C_2H_4O)_n$ (Merck, Germany)
12. Yellow food dye , commercial reagent grade, (Food yellow No.6, McCormick, USA)

All reagents and standard solutions were prepared using ultrapure water (Milli-Q® ultrapure water).

Soap solutions for various experiments were prepared by dissolving appropriate amounts of TX-100 in water. Some solutions were modified with other chemicals for different purposes.

Soap solutions in gas sampling experiments

A 2% TX-100 soap solution was prepared by dissolving 20 mL TX-100 in deionized water and making the volume up to ~800 mL. TX-100 is a nonionic surfactant but contains ionic impurities; these were removed by passage through a short mixed-bed ion exchange resin (Dowex MR-3) column. To this purified TX-100 100 mL glycerol was added and the volume then made up to 1 L. The final solution thus contains 10% glycerol and 2% TX-100.

In the sulfur dioxide sampling experiment, 10 mL of 3% v/v H_2O_2 was transferred to a 100 mL volumetric flask and made up to the mark with 10% glycerol + 2% TX-100; this solution was used for SO_2 sampling.

Soap solutions in vapor permeation experiments

A 5 % TX-100 soap stock solution was prepared by dissolving 5 mL TX-100 in deionized water and making up to 100 mL.

Solution of various glycerol contents (0, 10, 20, and 30 % v/v) in 5% TX-100 were prepared by adding 0 to 30-mL of glycerol to 5 mL of TX-100 before diluting with deionized water to 100-mL each.

Solutions of 1 and 3% w/v α-cyclodextrin (α-CD) in 10% glycerol + 5% TX-100 were prepared by dissolving 0.25 g and 0.75 g of α-CD, respectively, in stock 5% TX-100, adding 2 mL of glycerol and making the volume to be 25.00 mL with stock 5% TX-100.

TX-100 solutions in 0.05% and 0.5 % concentrations were prepared by diluting 1 and 10 mL stock 5% TX-100, respectively, in deionized water and adjusting the volume to the mark of 100 mL volumetric flask with deionized water.

Solutions of 5 and 10 % w/v α-cyclodextrin (α-CD) in 10% glycerol in 0.05% TX-100 were prepared by dissolving 1.25 g and 2.50 g of α-CDs, respectively, in 0.05% TX-100. Glycerol (2.5 mL) was added to it before adjusting volume with 0.05% TX-100 to be 25.00 mL.

H_2SO_4 Standards for soap bubble conductance measurement

1 M H_2SO_4 solution was prepared by diluting 5.5 mL concentrated sulfuric acid (98%) in 100 mL of water to be 1 M H_2SO_4. The prepared H_2SO_4 solution was acidimetrically standardized by titration with a secondary standard sodium hydroxide solution. This solution was kept as a stock standard solution.

In experiments for conductance/conductivity measurements, various concentrations of sulfuric acid solutions ($5 \times 10^{-4} - 5 \times 10^{-1}$ M) in 2% TX-100, 10% glycerol, were prepared by transferring 0.5 to 50 mL of the stock 1 M H_2SO_4 to 100 mL volumetric flask, before adding 10 mL of glycerol, following by adjusting the solution to the mark with an appropriate amount of purified TX-100 solution. The specific conductance values of the solutions were measured using a commercial cell of known cell constant (determined with standard KCl of known specific conductance).

5 mM Potassium hydrogen phthalate (KHP)

This solution was prepared by dissolving 5 g of KHP in 500 mL water.

$NaHSO_3$ in KHP buffer for SO_2 generation

It was prepared by dissolving 1.8 mg of $NaHSO_3$ in 250 mL of the KHP solution.

2.3 Making a spherical soap bubble

2.3.1 Setup to make soap bubbles

The bubble head was of annular tubular construction, as shown in Figure 2.1, having an inner soap solution delivery tube (0.57 mm inner diameter (i.d.) / 0.95 mm outer diameter (o.d.)) contained within an air delivery tube(glass tube, 1.8 mm i.d.). The two tubes are brought together by a T-fitting. The tip of the inner tube was recessed ~1 mm from the tip of the outer tube. At the tee, the tubes are sealed in place with epoxy adhesive. An aliquot of the soap solution is delivered by the solenoid pump and occupies the tip of the bubble head. The soap bubble is now created by flowing a measured amount of air through the outer tube.

Making the soap bubble and all subsequent measurements were conducted under computer control with instructions written in-house in SoftWire™ programming (Measurment Computing, Middleboro, MA) platform through a 16-bit A/D-D/A PCMCIA card (PC-Card-DAS16/16AO). The programming panel and the sequence diagrams of the program are shown in Figure 2.2 and 2.3, respectively. Figure 2.4 shows the setup for making the soap bubble and mesurements. The soap solution, purified 2% TX-100 in 10% glycerol was delivered from its container by solenoid valve pump (SVP). A short capillary tube (8.5 cm, 125 μm i.d.) is placed on the SVP outlet to dampen the impulse from the solenoid valve pump. The soap solution volume delivered at the bubble head was measured to be 5 μL/stroke. In the present experiments, a single pump actuation is enough to make the bubble. A short time (3 s) was allowed to elapse after the pump stroke for the soap solution to fill the bubble head tip. The solenoid valve (SV) outlet was then directed to the bubble head to let purified air flow to bubble head. The gas flows through a coiled 50-cm length

of polyurethane tubing (CT)(1.5-mm i.d., 3-mm that serves as a restrictor and dampener for the gas pressure. Bubble size was controlled by mean of the mass flow rate of air set in the mass flow controller and the length of time over which SV allows air to flow continuously to the bubble head.

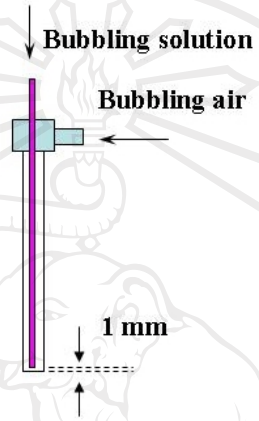

Figure 2.1 Annular tube-based bubble head

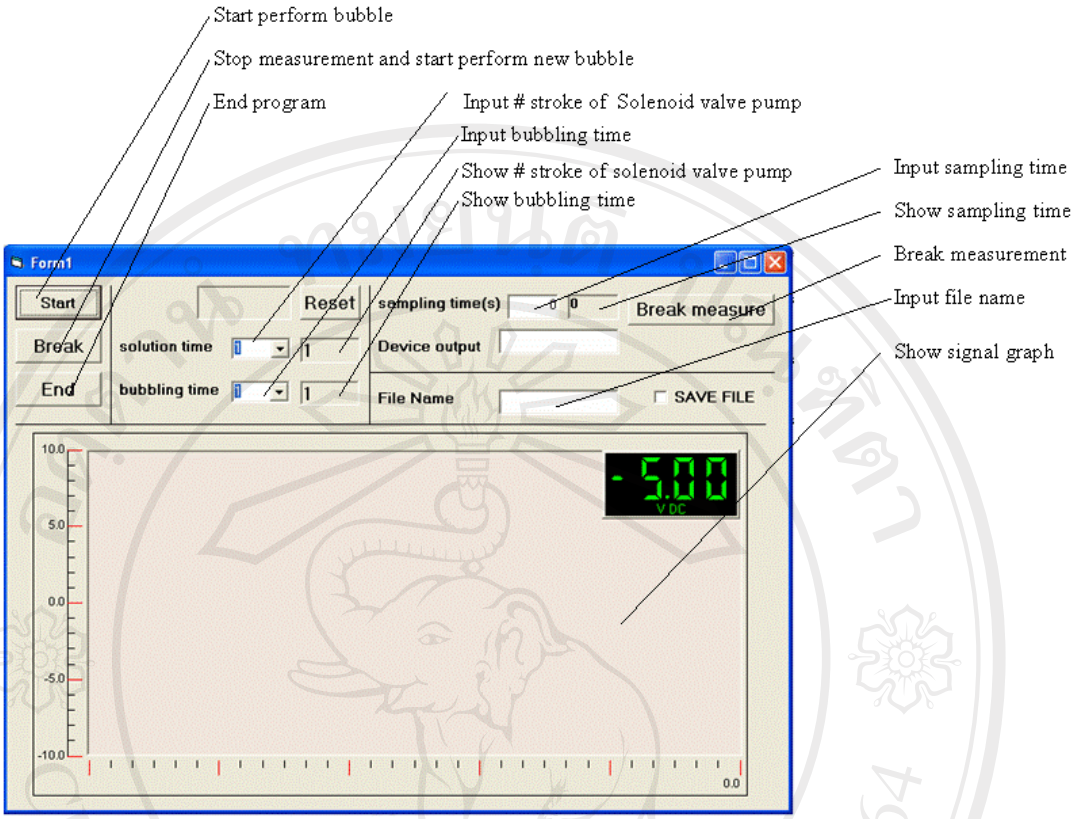

Figure 2.2 Panel: Soap bubble making program and measurement display

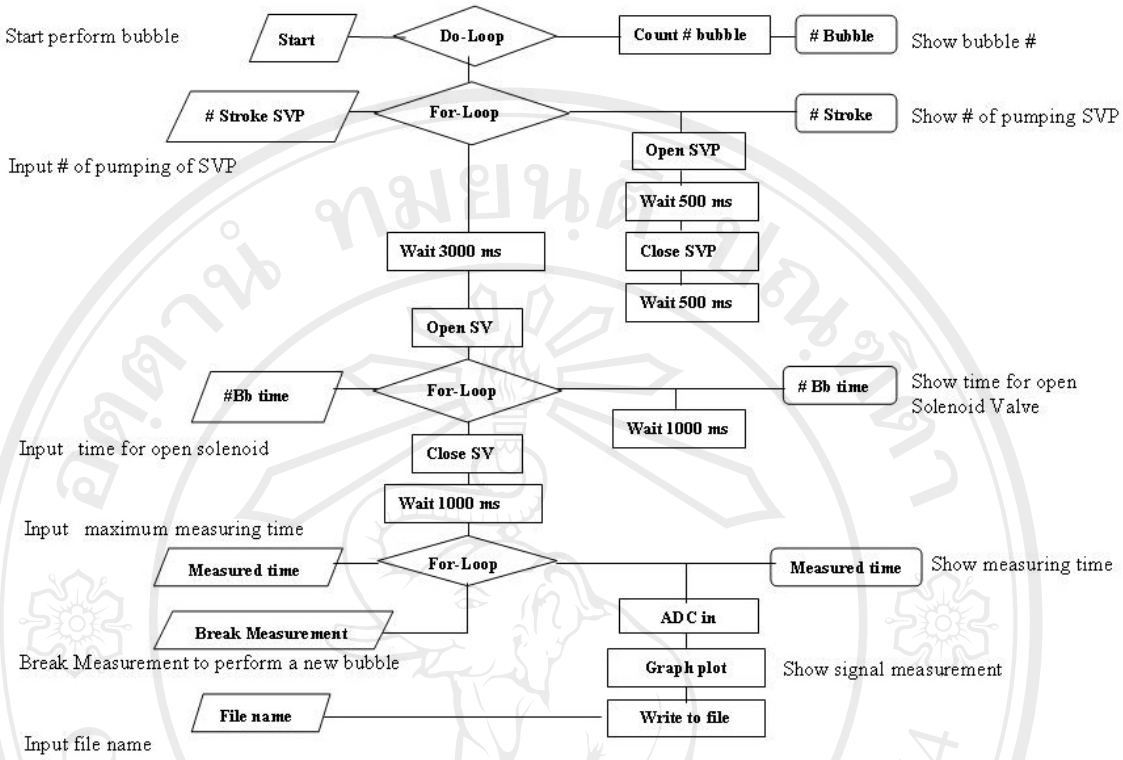

Figure 2.3 Softwire^{TM} programming sequence to make soap bubble and carry out measurements

Referring to Figure 2.4, the soap bubble was formed within a transparent otherwise sealed clear polystyrene box (10x10x12 cm WxLxH) which contained water W at the bottom in order to keep a humid atmosphere around the bubble. This prolongs the soap bubble lifetime. The conductivity measurement electrodes STE were made from 6 mm diameter type 316 stainless steel rods and were fabricated to fit snug in 0.75 mm wall thickness polyether ether ketone (PEEK) insulating sleeves (which could be moved horizontally in and out to accommodate different size bubbles). The electrodes were directly connected to a commercial conductivity

detector, which was calibrated for a cell constant of 1, i.e., the display read the absolute conductance in μS.

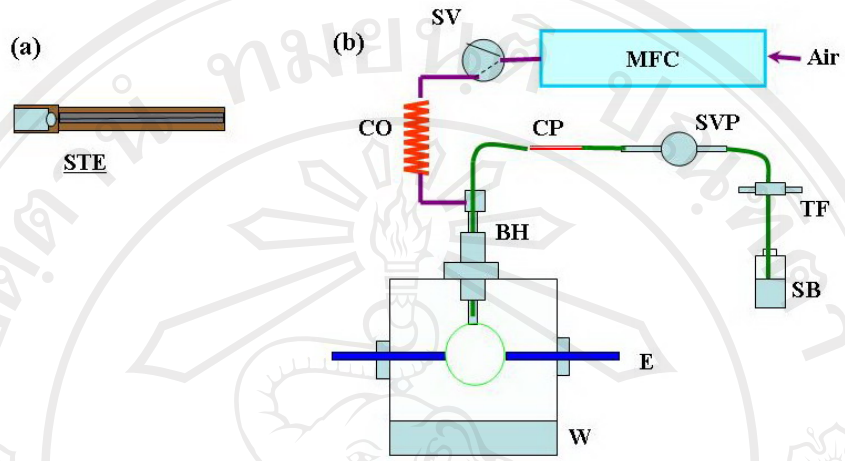

Figure 2.4 a) Stainless steel electrode. b) Bubble performing setup. The soap solution from solution bottle SB was delivered by using solenoid valve pump SVP passed through Teflon filter TF and PEEK capillary tube CP to annular bubble head BH. The constant flow of air from the mass flow controller passes through computer-controlled solenoid valve SV to the bubble head to form and inflate the bubble

2.3.2 Generation of SO_2 standard and detection of SO_2

Standard sulfur dioxide gas was generated by using the principle of Henry's Law equilibrium using a porous membrane tube as a solution-gas interface as shown in Figure 2.5. The general setup was similar to that described by Liu and Dasgupta for the generation of ammonia [108]. In this experiment, two streams of purified air were individually controlled by independent mass flow controllers. The first stream flowed at 200 mL/min through a copper coil maintained in a 20 °C bath for thermal equilibration and then through a porous polypropylene membrane tube that is wholly

contained in a glass bottle filled with 600 μM $NaHSO_3$ + 50 mM potassium hydrogen phthalate (pH 4) maintained in the same bath. The generation solution was changed every 3 days and was generally used within 18 H of preparation to avoid effects of oxidative decay of S(IV). This primary SO_2 concentration at the outlet of the membrane based source was measured by absorption into 0.3% w/v H_2O_2 contained in a glass midget bubbler for 30 min. The resulting sulfate formed was then measured by ion chromatography [109] and related to the SO_2 concentration.

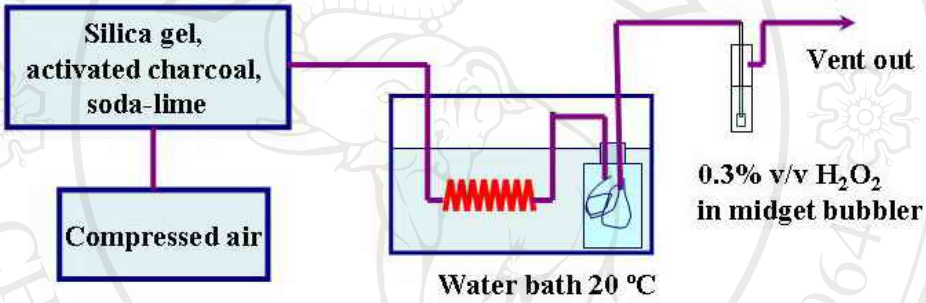

Figure 2.5 Schematic diagrams of SO_2 gas generation and sampling for standardization

2.4 Making planar soap films

Planar soap films were manually made on a film frame that was then put in a sealed chamber hereinafter called the permeation chamber. Details of making planar soap films and the associated set up are described below.

2.4.1 Permeation chamber

The chamber is made from a cylindrical polypropylene container sold for food storage (9.68 cm i.d., 7.75 cm tall); the entire arrangement is shown in Figure 2.6 and 2.7. A ring shaped support ledge (9.68 cm o.d., 9.15 cm i.d., 2 mm thick, machined from Perspex) fits tightly within the storage cylinder. The ring is pushed down into the chamber 1.62 cm from the top. The bottom of the container is then filled with a 4.61 cm deep layer of water to keep high humidity. The bottom is the donor chamber and gas inlet/outlet ports are provided approximately 1.05 cm below the ring insert. Similarly the receiver chamber is the portion above the ring and inlet/outlet ports are provided for this part 0.97 cm above the ring. The final and perhaps the most important part of the permeation chamber is the bubble holding frame (a 1-mm thick Perspex disc of 9.65 cm dia., that just loosely fits inside the box, this disc has 46.5x65.7 mm rectangular opening, resulting in an open area of 30.6 cm^2. In operation, the ring ledge is moistened with soap solution on the top, and the bubble holding frame is lowered on the ledge.

As shown in Figure 2.6, the permeation chamber is divided by the soap film into an upper receiver compartment (computed volume 94.7 mL) and a lower donor compartment, the effective volume of which was controlled by water level. For all of the present experiments, the effective volume of the donor chamber computed from chamber diameter and height of compartment space from water level to ring disc was 111.6 mL.

There are inlet and outlet ports for gas to flow in and out in each compartment. For the donor compartment, the inlet hole was connected to a α-pinene vapor stream while the outlet was simply vented to the atmosphere. For the receiver compartment,

the one port was connected to a suction pump. This outlet port was closed during permeation study and will be operated for suction of trace amount of vapor out of the chamber after finish permeation study. while the another port was connected to a coil of Tygon tubing (50 cm length of 6 mm id tube) and open to atmosphere during permeation study.

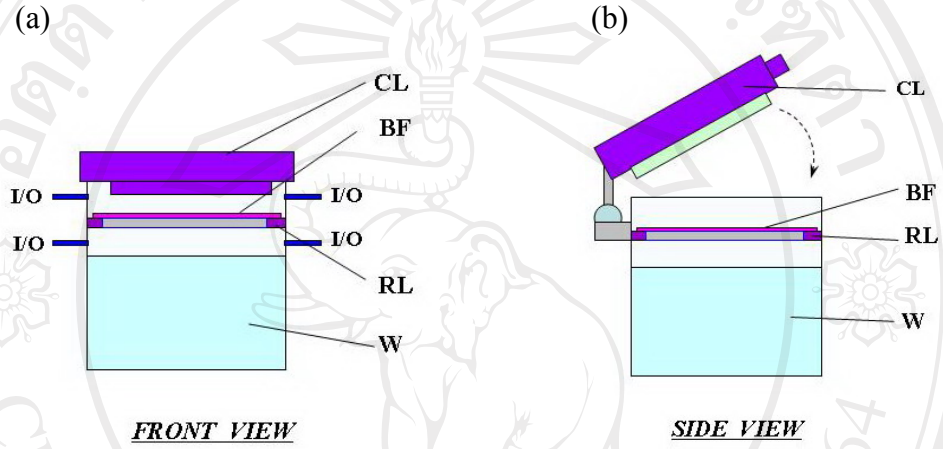

Figure 2.6 Schematic diagram of permeation chamber. a) Front view, CL=cover lid, BF= Perspex bubble frame, RL= Perspex ring ledge, W= water, I/O = inlet/outlet for vapor flow in/out. b) Side view

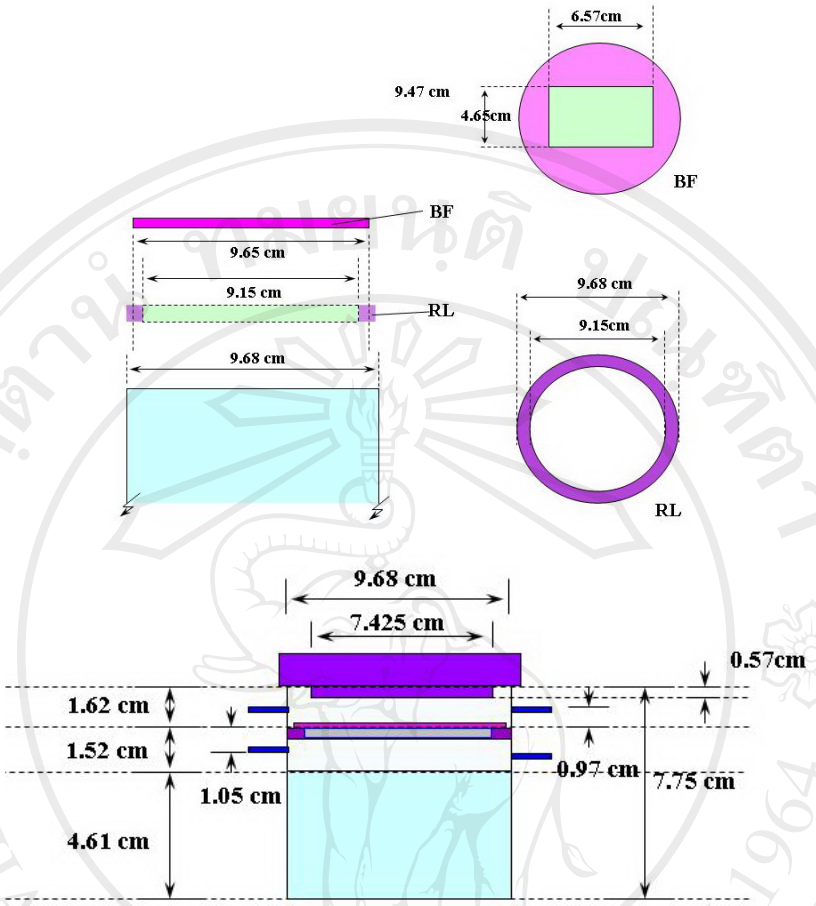

Figure 2.7 Dimensions of permeation chamber and 1 mm thick Perspex frame and 2 mm thick perspex ring ledge which attached in the chamber

2.4.2 Making a planar soap film

Figure 2.8 illustrates the making of the planar soap film. First a thin layer of soap solution is used to moisten the top of the ring ledge RL. The bubble frame BF is then gently placed on it – it is sealed to the ledge merely by the adhesive force of the soap solution. A thin solid Perspex plate (50 x 70 x 1 mm) is dipped in the 10% glycerol-5%TX-100 soap solution. It is then taken out and this soap solution wetted plate is slid across the open area of BF whereupon a soap film is formed on the open window. The chamber lid can now be closed. The film lifetime is prolonged in a humidified atmosphere by using water at the bottom of permeation box.

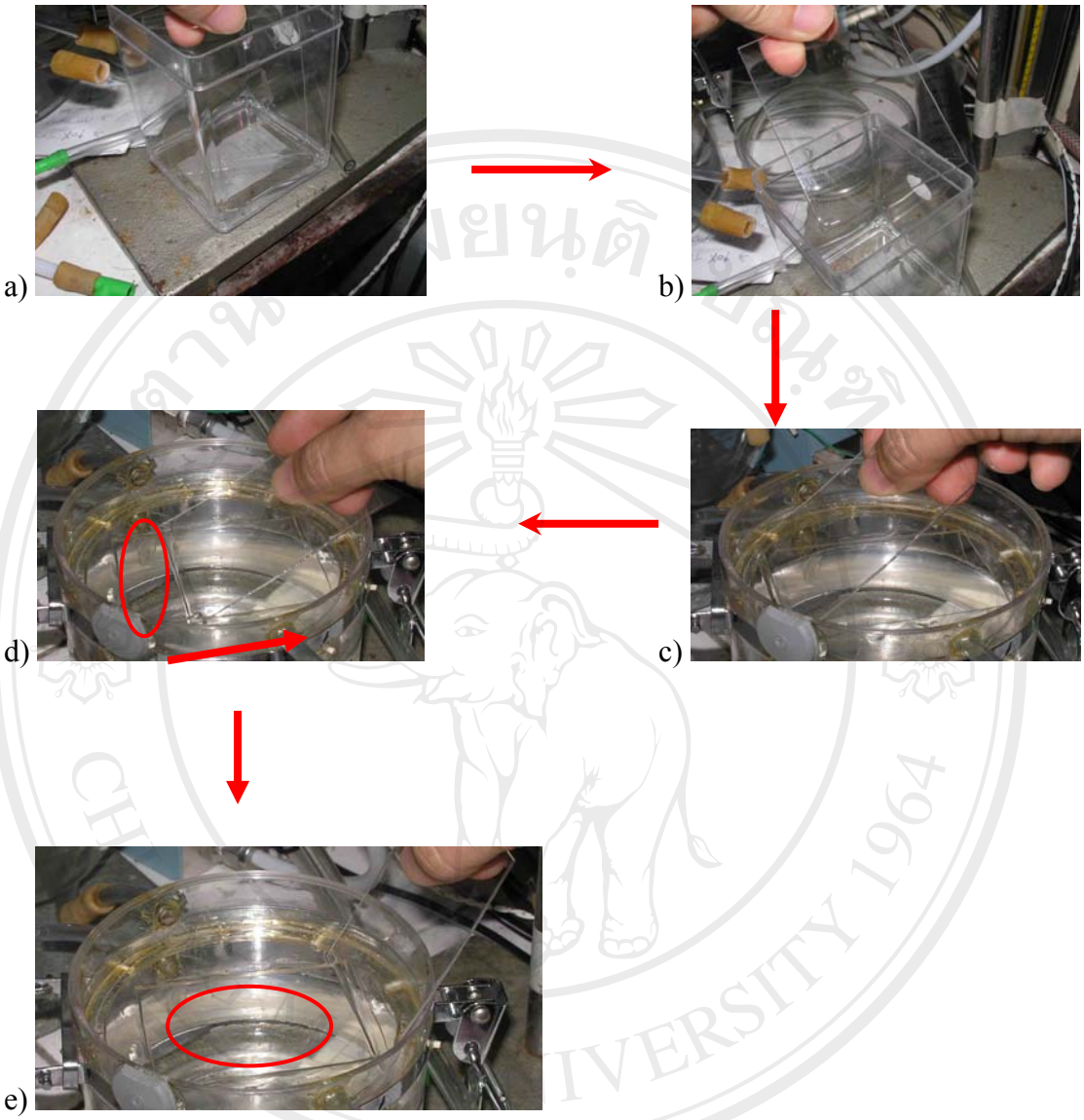

Figure 2.8 Making soap film: a) dip plate in soap solution b) lift soap solution soaked plate, c) and d) sliding Perspex plate on Perspex frame e) soap film is formed on the frame in the permeation chamber (*Note the liquid film on the edge of window of plastic frame*)

2.4.3 Standard α-pinene vapor generation

Setup of alpha pinene vapor generation is depicted in Figure 2.9. Purified air was split into 2 lines; first line which was controlled air flow rate by mass flow controller, MFC1, flow through copper tube (for air temperature adjustment) and diffusion chamber which contained 2 vials of (+) α- pinene and (-) α- pinene. Both of the 2vials were filled with liquid α- pinene and let its vapor diffused through a 1 mm diameter hole on lid of the vials. Both copper coil and diffusion chamber were immersed in a constant temperature water bath (40 °C). With constant flow rate of air through a diffusion chamber, a constant concentration of α-pinene vapor in the outlet was expected. The exact α-pinene vapor concentration was calculated from weight loss of both vials which were weighted everyday.

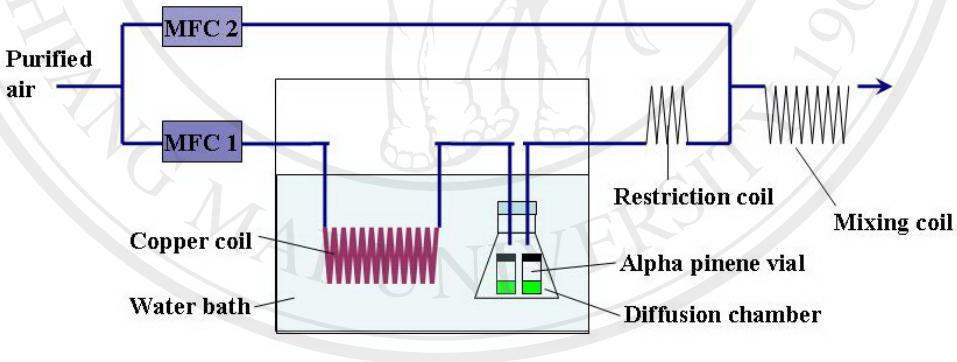

Figure 2.9 Setup for α-pinene vapor generation. MFC1= mass flow controller-1, MFC2= mass flow controller-2

From α-pinene weight loss (1.28×10^{-3} g/h and 1.23×10^{-3} g/h of plus (+) and minus (-), respectively) and flow rate of purified air which flow through alpha pinene vials (116.8 mL/min), the original vapor concentration of both chiral forms could be calculated to be 1.83×10^{-7} g/mL and 1.76×10^{-7} g/mL for plus (+) and minus (-)

forms, respectively. The outlet of diffusion chamber connected through a restriction coil to the second purified air line of known flow rate controlled by mass flow controller, MFC2. The second air line was used as dilutor. Various concentrations of pinene vapor concentration could be produced by varying flow rate ratio of both lines.

2.4.4 SPME-GC for α-pinene detection

Concentration of α-pinene vapor used in permeation chamber was determined by static sampling with SPME for 30 s, and analysis by using gas chromatograph with Cyclosil B column and frame ionization detector (FID) detector (at 250 ºC). With using operating condition of initial temperature 55 ºC, increasing temperature rate 2 ^{o}C/min, final temperature 180 ºC, and nitrogen carrier gas linear gas velocity 25 cm/s, the retention time of (-) and (+) alpha pinene is 14.31 and 14.63 min, respectively.

Validation of SPME-GC method by using known concentrations of α- pinene and under the same sampling and analysis condition as in permeation study has been carried out. For SPME-GC calibration in this experiment, the α-pinene vapor stream was flown though U-tube as shown in Figure 2.10 for 30 min. Then the flow was stopped and both ends of U-tube were closed to make a static condition in sampling similar to that was performed in a permeation chamber.

Figure 2.10 U-tube for sampling of vapor in SPME-GC calibration

2.4.5 α-pinene permeation study

Firstly, the permeation chamber was cleaned by operating sucktion pump for 15 min to suck trace amount of vapor from the chamber, and humidified air was flow through the chamber for 10 min in order to make a humidified atmosphere in the chamber.

Then, a soap film was made on the frame, and the box cover was closed. The α-pinene source (original concentration without dilution) was connected to the inlet port of the donor compartment while the outlet port was opened to the atmosphere. The α-pinene vapor was allowed to flow through the donor compartment for 3 min at 117 mL/min and then the α-pinene source was immediately disconnected.

Concentrations of the two forms of α-pinene were measured by placing the SPME fiber for 30 s at the different position as follow: (A) in the donor chamber, (B) in the receiver chamber and (C) in a U-tube placed at the α-pinene vapor inlet line as shown in Figure 2.11 and 2.12. Because we had only one SPME fiber available, the

sampling in the different places can not be done at the same time. The implicit assumption is that the experiments are repeatable when identical conditions are used.

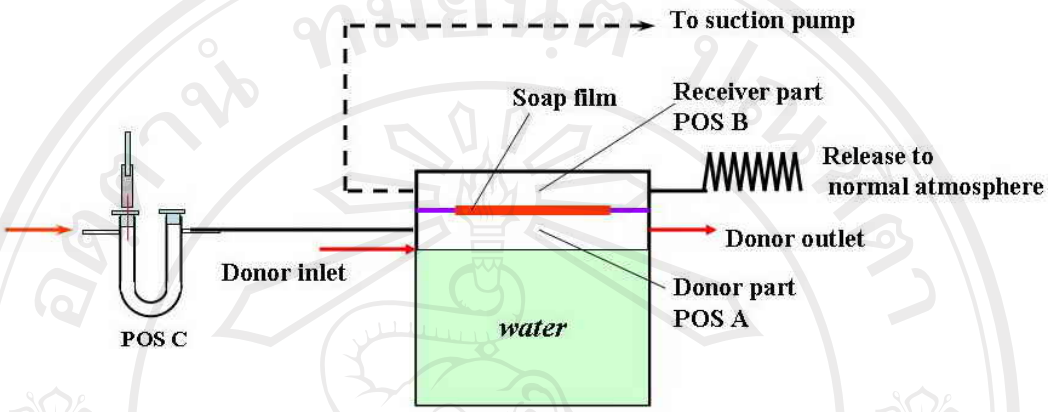

Figure 2.11 Sampling locations: (A) donor chamber, (B) receiver chamber, and (C) in U-tube placed in-line in the source stream (*Note: a dash line is connection to a suction pump operated to clean permeation chamber when finish permeation study*)

Figure 2.12 Photograph of permeation chamber while SPME sampling is being carried out in receiver chamber