

# Small Bubbles Oxygenation Membrane

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**ABSTRACT:** Large bubbles emerge from porous membranes with small pores because the emerging bubbles spread on the membrane surface before they detach from the surface. If the sessile bubble contact angle ( $\theta$ ) is less than  $45^\circ$ , no spreading occurs, and the bubble size is determined by the size of hole. Even in this case, the equivalent diameter (of spherical bubble) is significantly larger than the pore diameter due to the bubble formation mechanism. If  $\theta > 45^\circ$ , the spreading of the emerging bubble on the surface occurs, and the bubble size is determined by the size of base of a sessile bubble, which depends on the value of  $\theta$ , and is independent of the pore size. The equivalent diameter of a bubble could be greater in order of magnitude than the pore

diameter. The same principle applies to the bubble formation from an inclined surface; however, the bubble formation is more complicated because of drifting of a developing bubble out of the orifice and the merging of sliding bubbles. In order to create small bubbles, it is necessary to create small orifices on a hydrophilic surface, of which  $\theta < 45^\circ$ , and two orifices should be separated beyond the maximum diameter of emerging bubble. A horizontal flat surface is the best for the creation of small-sized bubbles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 387–398, 2003

**Key words:** coating; membranes; plasma polymerization; surfaces

## INTRODUCTION

The membrane in a broad sense is a thin layer that separates two distinctively different phases. No characteristic requirement, such as polymer, solid, etc., applies to the nature of materials that function as a membrane. A liquid or a dynamically formed interface could be also dealt as a membrane. Although the selective transport through a membrane is an important feature of membranes, it is not necessarily included in the broad definition of the membrane. The overall transport characteristics of a membrane depends on both the transport characteristics of the bulk phase as well as the interfacial characteristics between the bulk phase and the contacting phase or phases, including the concentration polarization at the interface.

Dealing with polymer membranes, “membrane science” is nearly synonymous to the transport mechanisms through the bulk phase of membrane, and the importance of interfacial aspects of membranes are often not recognized or totally ignored. In such a narrow window of “membrane,” the porous membrane is not considered as a membrane if the pore size is beyond some arbitrarily set range of preference. For instance, a plate with a hole of which diameter is 0.25 mm, which is used in this study, is not considered as a membrane. However, porous membranes with mil-

limeter-sized holes function well in the transport of gases into liquid phase, which is an important chemical engineering process.

A polymer membrane employed in water aeration device is a typical case for this kind of membranes. A rubber film with numbers of slits functions as a thin layer that separates the gas phase and the liquid phase, which allows the transfer of the gas into the liquid phase in a controlled manner. Such a film is appropriately termed as aeration membrane.

In the domain where the entity that is transported through a membrane is immiscible or not completely soluble in the contacting (exit) phase, such as the case of air or oxygen in water, the interfacial factor becomes overwhelmingly important over the transport characteristics of the bulk membrane phase. It is important to recognize that the surface of porous membrane consists of the solid phase and the gas phase (in the pore diameter exposed to the interface), and the interfacial aspect of the solid surface dominates the behavior of the gas phase that expands out of the pore.

The basic factors involved in this case are examined in this article for oxygenation of liquid water by small-sized air bubbles emanating from a porous membrane. In order to identify basic steps of bubble development and detachment from the membrane surface, a model membrane, which consisted of a well-defined hole created on a stainless steel, was used.

## EXPERIMENTAL

Two articles were presented on the subject of the role of interfacial tension in the formation and the detach-

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ment of air bubble emerging from a single hole placed on a stainless steel plate.<sup>1,2</sup> These studies are the main reference studies in this article.

A circular and clear-edged hole (0.55 or 0.25 mm diameter) was created on a stainless steel sheet. The surface of the sheet was coated by cathodic plasma polymerization of trimethylsilane (TMS) or a mixture of TMS and oxygen, whose ratio was the parameter to control the surface energy of the surface that surrounds the hole.<sup>3</sup> After a series of experiments with a membrane (stainless steel sheet with a hole), plasma coating was mechanically removed, and another plasma coating with different surface energy was applied. Thus, membranes with exactly the same hole with different surface energies were prepared one at a time.

The bubble volume was calculated from the total volume of air passed through a hole and number of bubbles, which was counted by playing the recorded videotape, in a given time. The bubble diameters, surface to volume ratio, etc., are derived from the calculated bubble volume, assuming the spherical bubble, although bubbles in water are far from a sphere as seen in the figures presented. The details of experimental procedures were presented in refs. 1 and 2.

## BACKGROUND

### Bubble vs. membrane oxygenation

The oxygenation of water or water suspension such as blood can be done by (1) blowing oxygen gas into the liquid or via a porous membrane, and (2) bubble-less oxygenation via a gas-permeable (nonporous) membrane. Both methods have advantages and disadvantages, which seem to be complementary, and the choice is entirely dependent on the nature of the application. One feature could be an advantage in one application, but a disadvantage in another application, and vice versa. Some characteristic factors for both processes could be examined by using the cases of blood oxygenation and oxygenation (aeration) of water.

### Blood oxygenation

Oxygenation of blood can be achieved by bubbling oxygen through blood contained in a vessel, which is a part of an overall flow system of blood. This process is practiced in a bubble oxygenator. Oxygen literally bubbles through blood retained in the vessel. The advantage of this approach is that the process is simple and the oxygenation is fast and efficient because an oxygen bubble contacts with many red blood cells before it leaves the blood phase. It should be emphasized that the essential step of blood oxygenation is

the transfer of oxygen to red blood cells, which differs significantly from oxygenation of liquid, e.g., water. The disadvantage of this approach is that bubbling of oxygen, particularly with large bubbles at a high flow rate, could cause trauma to red blood cells and hemolysis (breakdown of red blood cells).

Bubbles could be created by multiple of capillaries or holes created on a surface. However, the formation of small bubbles on a membrane surface, particularly at low flow rate, is not as easy as it might be conceived. Furthermore, the basic principle for how to make small bubbles had not been available until the two reference papers were published in 1994.

Nonporous membrane carries out bubble-less oxygenation of blood—i.e., no bubble emerges from the membrane surface. The dissolved oxygen is transferred from the membrane phase to the liquid phase, which contacts the membrane surface. Characteristic oxygen transfer rate (per unit membrane area) could be high enough to cope with requirements for blood oxygenation processes. The advantage of this approach is that no gas phase oxygen contacts with blood, and consequently the trauma caused by bubbling could be greatly reduced. This process is practiced in the membrane oxygenator.

The disadvantage of this approach, on the other hand, is that the concentration polarization at membrane surface becomes the rate-determining step as the membrane transport rate increases. Because the transfer of oxygen to liquid phase precedes the transfer of oxygen to a red blood cell in most cases, it is necessary to maintain a certain flow rate of liquid at the membrane/liquid interface and/or to provide a device to create mixing of oxygenated red blood cells and unoxygenated red blood cells in order to take advantage of high oxygen transport rate through the membrane. These necessary actions increase the trauma to red blood cells and negate the advantage of membrane oxygenation. Another disadvantage is that a unit volume of blood is exposed to a much larger surface area of a foreign body (membrane surface) compared to that in a bubble oxygenator. Considering pros and cons of these two approaches, blood oxygenation via small bubbles at low flow rate seems to be a very viable approach if one could create many small bubbles at a low flow rate regime.

### Oxygenation of water

Oxygenation or aeration of water is essentially the same process as the blood oxygenation, except the requirements are much less stringent because oxygen transfer occurs to the liquid phase. Most aeration is carried out by bubbling air into water by pipes or membrane devices. Aeration membranes are essentially sheets of rubber with many holes in form of slits. The main functions of membrane are (1) providing

numbers of holes and (2) providing valve mechanism to prevent flooding of the pipe system when the system is depressurized. Under applied pressure, the membrane expands and the slit opens. When the aeration system is depressurized, membrane contracts and the slits close by the hydrostatic pressure of water.

The advantage of membrane device over the direct bubbling from pipes is the reduction of energy necessary to oxygenate water. Many of large bubbles leave water phase without oxygenating water. The efficiency increases with the surface to volume ratio of a bubble. Thus, the creation of small bubbles in the low flow rate regime should increase the efficiency of oxygenation and reduces the energy consumption significantly.

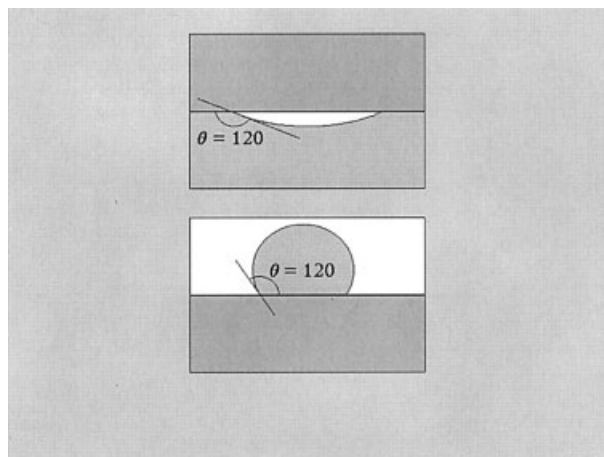
Previously known factors that control size of bubble

In the study of the bubble formation process carried out in the past, little attention has been paid to the influence of the nature of the surface. The lack of attention to the influence of the surface is probably due to the fact that most-of work on the bubble formation was carried out with a single capillary tube in water, which has the minimum surface area around the orifice.<sup>4–10</sup> Many researchers had reported (capillary experiments) that liquid surface tension, contact angles, and orifice orientation (tilt angle) have negligible effect on bubble formation.<sup>9,11,12,13</sup>

It has been indicated that the size of a bubble slowly formed at a submerged, horizontal, circular orifice, and detached by buoyancy alone is controlled by (1) the *size of orifice* and (2) the *liquid surface tension*.<sup>11,12</sup> (See Fig. 2 for the distinction of the liquid surface tension,  $\gamma_{lv}$ , the surface tension,  $\gamma_{sv}$ , and the interfacial tension,  $\gamma_{sl}$ .) Dealing with oxygenation of water, only the size of hole remains as the parameter that could be used to control the size of bubble emerging from the surface of an aeration membrane, if one accepted the above principle. One of the authors (JNL), while working at a manufacturer of aeration equipment, made a serious effort to reduce the size of bubble by creating small holes on the aeration membrane with no avail. The size of bubble emerging from much smaller holes was practically identical to the normal membrane with larger holes.

#### Sessile droplet contact angle vs sessile-bubble contact angle

The contact angle of water on a surface, in the context of wettability of the surface, can be measured by the sessile droplet method and the bubble injection method. The former measures the contact angle of a water droplet on a surface, and the latter measures the contact angle of an air bubble trapped below the surface immersed in water. The contact angle is generally



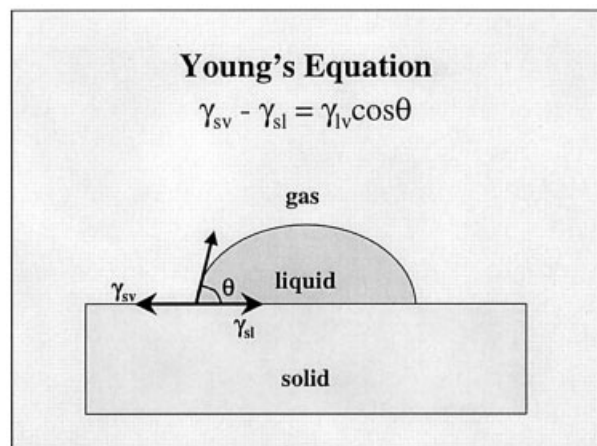
**Figure 1** Contact angle of a water droplet and of an air bubble trapped under a surface.

defined as the angle between the surface and liquid. Figure 1 depicts contact angles involved in the two different methods. Figure 2 depicts force balance at three-phase line for a sessile droplet and for a sessile (air) bubble.

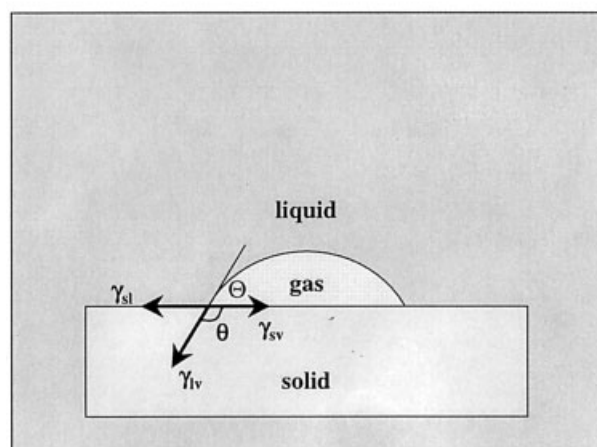
For a sessile bubble, Young's equation still holds. However, it should be recognized that the location and the direction of  $\gamma_{sl}$  and  $\gamma_{sv}$  are different from the case for a sessile droplet. Figure 2(b) depicts a cross-sectional view of an air bubble on a solid surface immersed in liquid water (sessile bubble). The angle  $\Theta$ , which is generally recognized as contact angle in the case of a sessile droplet, is the supplementary angle of the contact angle  $\theta$  in the case of a sessile bubble. Thus, a surface that gives a large contact angle of water droplet gives a small  $\Theta$  when a bubble develops on the surface immersed in water—i.e., an air bubble spreads on a hydrophobic surface.

The bubble injection method utilizes a sessile bubble below the surface. It is nearly impossible to measure the sessile bubble contact angle on top surface of a sample, whose contact angle is to be measured, because the buoyancy works in the direction to lift the bubble. It is more difficult to measure the air bubble contact angle, and consequently the bubble method has not been widely used. Although the two methods should yield the identical contact angle, the values obtained by the two methods could deviate significantly depending on the perturbability of the surface by water as described below.

The discrepancy is generally small in the case of hydrophobic polymer surface but could be very large in the case of hydrophilic polymer surface. For example, the sessile droplet contact angle of a gelatin hydrogel (water content ca. 95%) surface is over  $90^\circ$ , while the contact angle by the air bubble injection method is below  $15^\circ$ .<sup>14,15</sup> The extent of this discrepancy, however, could be estimated by the hysteresis of



(a)



(b)

**Figure 2** Contact angle of (a) a sessile water droplet and (b) a sessile air bubble.

sessile droplet advancing and receding contact angles.<sup>16</sup>

What is important in the bubble formation process is the sessile bubble contact angle on the top surface (not at the bottom surface). Therefore, it is necessary to estimate the sessile bubble contact angle on the top surface by the sessile droplet contact angle. If the membrane surface is highly perturbable, this becomes an impossible task, as it could be understood by the example of gelatin gel.

A well-defined hole on a nondeformable and unperturbable surface is the prerequisite for the fundamental study. The selection of a simple one-hole membrane was the mandatory step, but not a simplification

of complex phenomena. The selected system has the following important features.

The use of stainless steel sheet

1. A laser beam can create a perfect circular hole.
2. The wall of hole is perfectly perpendicular to the surface, and the edge is precise and free of deformation or irregularity.
3. The sheet does not deform under applied air pressure, and the hole does not change its size and shape when air pressure is increased for higher flow rates.

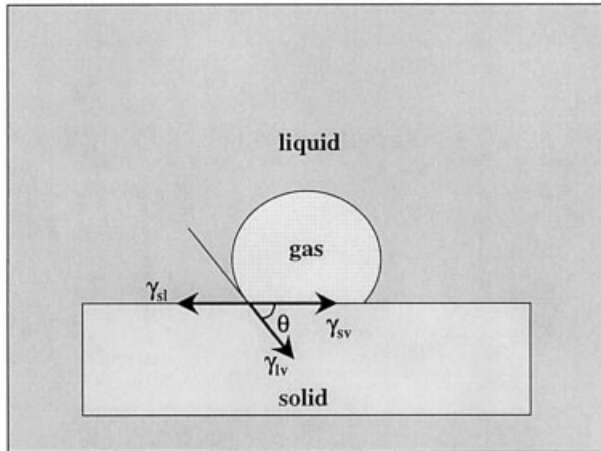
Surface modification by application of plasma polymers

1. The surface energy can be tailored by changing the ratio of oxygen to trimethylsilane in plasma polymerization. Depositing nanofilm (e.g., 50 nm) of plasma polymers with different surface energy can easily create the surfaces with various contact angles of water, in a wide range.
2. The same hole can be used repeatedly by changing the plasma-polymerized nanofilm.
3. The sessile bubble contact angle on the top surface can be estimated by the sessile droplet contact angle, because hydrophilic surfaces created by the plasma polymerization are imperturbable and show little discrepancy between advancing and receding contact angles. Thus, the sessile droplet contact angle can be used to estimate the sessile bubble contact angle on the membrane surface.

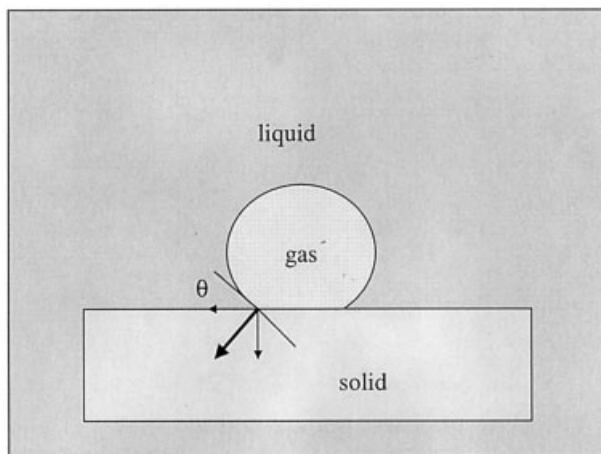
## RESULTS AND DISCUSSION

As seen in the sequence of still pictures presented, a spherical bubble with a finite contact area on the membrane surface develops as soon as the boundary surface between air and water passes the orifice. It is important to note that the spreading of air phase on the membrane surface and the development of the bulk of a bubble occur simultaneously. However, a constant base is established in the very early stage, and the major portion of bubble development occurs using the fixed contact base. The base area differs depending on the interfacial tension between water and membrane surface. The force balance that is important to understand the bubble development can be shown as depicted in Figure 3.

Figure 3(a) depicts the force balance at the three-phase line for a developing bubble (interfacial force balance). Figure 3(b) depicts the parallel and perpendicular components (with respect to the membrane surface) of the force due to the air pressure inside the



(a)



(b)

**Figure 3** Force balance at the three phase line: (a) interfacial tension and (b) gas pressure.

bubble at the three-phase line. The force that expands the bubble at the three-phase line can be expressed by  $\gamma_{lv} \cos(\pi - \theta) = \gamma_{lv} \sin \theta$ , from Figure 3(b). The force that contracts the contact area can be expressed, from Figure 3(a), by  $\gamma_{lv} \cos \theta$ . The balance between these two forces determines the size of base for a sessile bubble that develops on membrane surface.

The critical factor is whether the size of base for a sessile bubble is larger or smaller than the size of orifice. If the size of orifice is larger than the base of a sessile bubble, a sessile bubble does not form. Since no one would anticipate creation of small bubbles from a large orifice, this domain is clearly beyond the scope of this study. For small size orifices, whether an air bubble emerges from the orifice or emerges from surface is

the critically important factor, which is determined by the balance of  $\cos \theta$  and  $\sin \theta$ .

### The domain where the size of bubble is controlled by the size of orifice

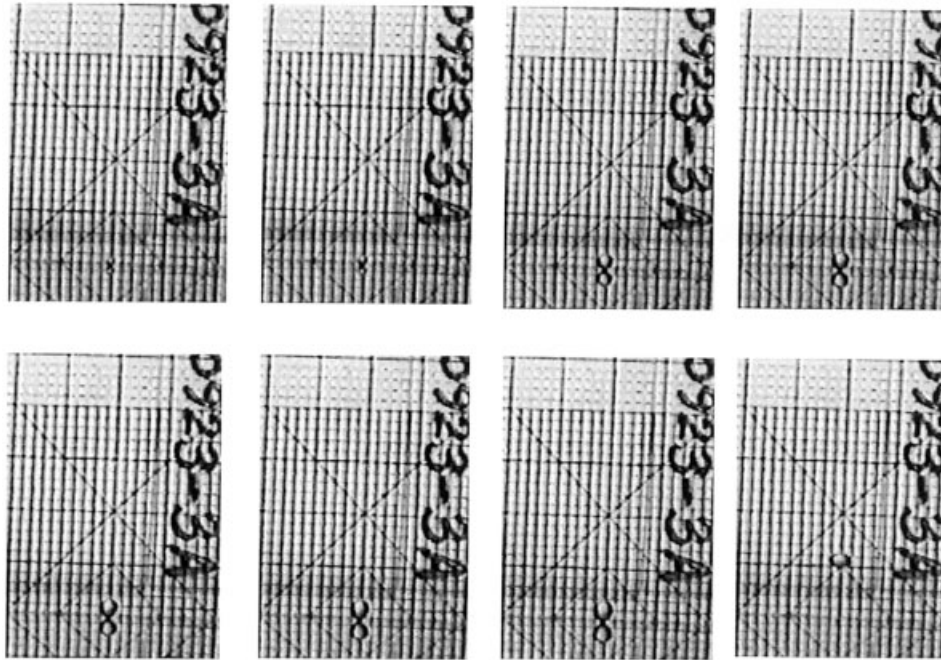
If the sessile bubble contact angle  $\theta < \pi/2$  (hydrophilic surface),  $\sin \theta < \cos \theta$ . Accordingly in this domain, an emerging bubble cannot expand its contact base beyond the area of the orifice. In this domain, a bubble develops by using the area of the orifice as the contact base, maintaining the spherical shape of bubble, and detaches from the orifice. The ultimate size of bubble depends on the volume, which creates enough buoyancy to detach the bubble from the edge of the hole. In this domain, the bubble volume is determined by the size of the orifice, and is independent of the contact angle of the surface (below  $\pi/2$ ) that surrounds the orifice.

The formation of bubbles in this domain can be seen by sequentially captured images of bubbles shown in Figure 4. The picture of a bubble emerging from a hole appears as if two bubble are attached, because the bottom half is the reflection of the bubble (mirror image) on the surface. The separation of two images is the indication of the bubble detachment from the surface. (The double images appear in all pictures shown in subsequent figures. A 1 mm grid is placed as a reference of size. If the grid plate is not perfectly parallel to the surface, two nonparallel lines show up as seen in Figure 6.) A bubble maintains the spherical shape up to the point where it detaches from the orifice.

### The domain where the size of bubble is independent of orifice size

In the range  $\pi > \theta > \pi/2$ ,  $\sin \theta > \cos \theta$ , and an air bubble emerging from an orifice expands its contact base beyond the orifice. When the contact angle of water  $\theta$  is not too far from  $\pi/2$ , the formation of an air bubble follows the same mechanism as the case of nonexpanding case shown in Figure 4, except the base of bubble is larger than the orifice. Figures 5 shows sequentially captured images of bubbles in this case. The developing bubble maintains the shape of spherical bubble attached to the surface until just before the detachment occurs. The contact area of a bubble shrinks to the size of orifice just before the detachment occurs, and the shape changes to that of "hot-air balloon." The exact moment of detachment was not captured due to the limitation of shutter speed. The size of the next bubble following the detachment suggests that the detachment took place at the orifice.

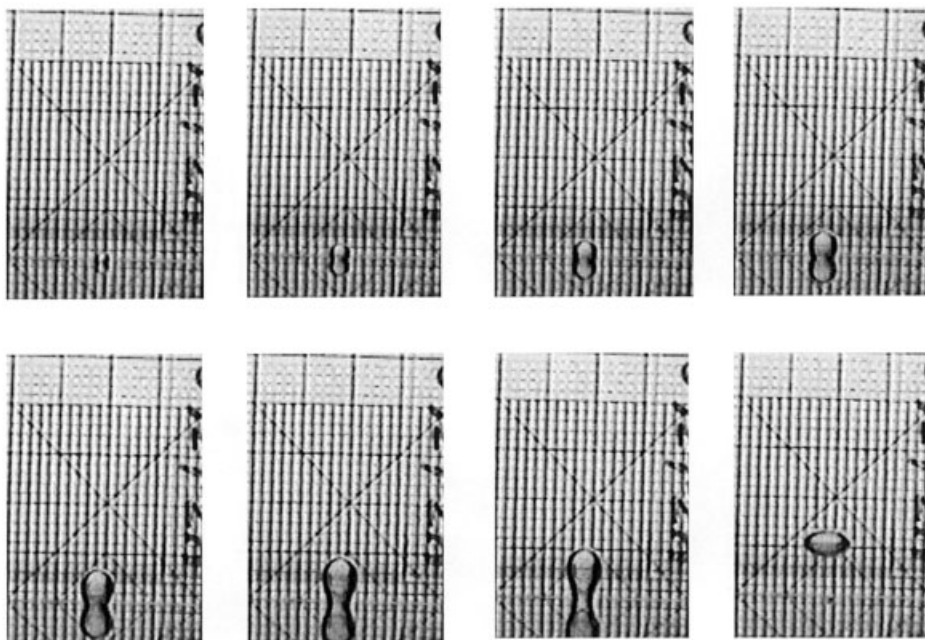
In the domain where  $\theta$  is equal to or greater than  $\pi$ , the shape of a developing bubble becomes a half sphere when the maximum contact area is established



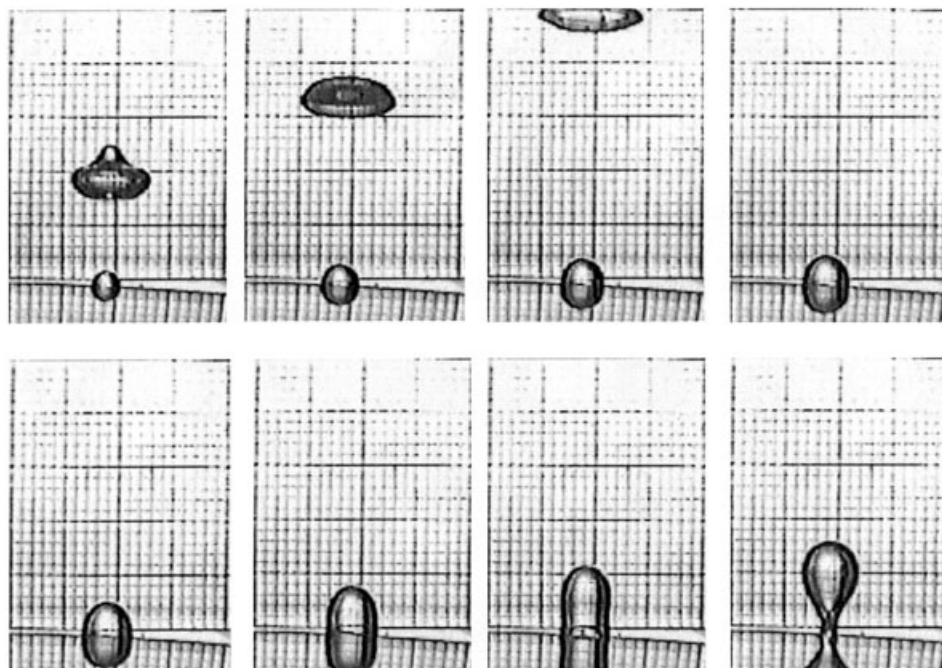
**Figure 4** Bubble formation without expanding the contact base of a bubble beyond the orifice: contact angle of water  $5.0^\circ$ , orifice diameter 0.25 mm, air flow rate 0.26 mL/m, and bubble volume 0.0050 mL/bubble.

in the early stage of bubble development. After this point, a cylindrical bubble with half-sphere cap develops, because the bulging of bubble beyond the contact base cannot occur due to the contact angle. The bubble, from this point on, expands its volume mainly by increasing the height of the cylindrical part. As buoy-

ancy increases, the size of attachment area starts to decrease, and the shape of bubble changes to that of a hot air balloon also in this case. The bubble formation in the domain  $\theta \geq \pi$  can be seen in Figure 6, which are sequentially captured images of a bubble emerging from an orifice (diameter 0.25 mm) placed



**Figure 5** Bubble formation with expanded base of a bubble beyond the orifice: contact angle of water  $70.0^\circ$ , orifice diameter 0.55, air flow rate 0.56 mL/m, and bubble volume 0.037.



**Figure 6** Bubble formation with cylindrical expansion: contact angle of water 99.7, orifice diameter 0.25 mm, air flow rate 0.82, and bubble volume 0.092 mL/bubble.

on a very hydrophobic surface. It should be noted that the base of the bubble is nearly 10 times greater than the diameter of the orifice.

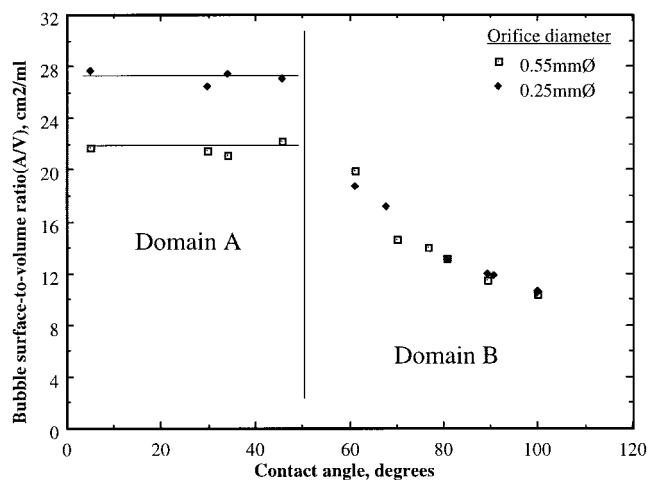
It should be reiterated here that the bubbles shown in Figures 4–6 emerged from the identical orifice. The identical orifice plate was used in these experiments. The only difference was the surface energy of the plate, which changed the characteristic sessile bubble contact angle.

These figures are convincing demonstration of the principle that the size of bubble is determined by the size of the base of sessile bubble. There are two basic boundary conditions for this principle: (1) there must be enough surface area, on which the contact base can develop, and (2) the size of orifice must be smaller than the maximum size of the contact base. Nearly all past studies employed experimental conditions that do not fulfill these requirements for small bubble formation, and hence the principle described in this article had not been found.

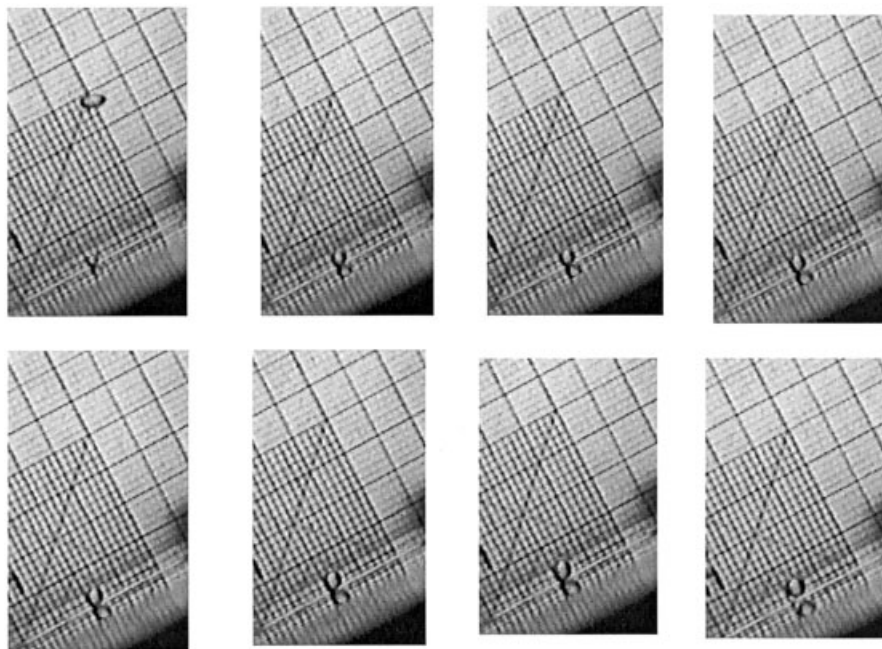
Figure 7 depicts the relationship between the size of bubble and contact angle (degree) of water on the surface, which surrounds the orifice. In order to show the difference due to the size of orifice clearly, the surface area to volume ratio  $A/V$ , which is an important parameter in gas–liquid reactions, rather than  $V$  or bubble diameter, is used in this plot. Figure 7 clearly shows the two distinctively different domains: (A) the orifice size controlled domain and (B) the interfacial tension controlled domain. Also, The demarcation line is contact angle of water 45°. In the

latter domain, larger bubbles emerge from a small orifice and the bubble size is independent of the orifice size.

The effect of size of orifice can be seen only in domain A. This is the reason why any attempt to reduce bubble size by making the size of orifice small would fail, because most of organic polymers used for aeration membranes are relatively hydrophobic (contact angle of water being greater than 45°). Without reducing the contact angle of water to less than 45°,



**Figure 7** Domains of bubble formation. Domain A: bubble volume is controlled by the size of orifice; domain B: bubble volume is controlled by the interfacial tension.



**Figure 8** Bubble formation from a tilted orifice plate: tilt angle  $30^\circ$ , contact angle of water  $41.5^\circ$ , orifice diameter 0.55 mm, air flow rate 1.98 mL/m, and bubble volume 0.011 mL/bubble.

the small size orifices do not produce small size bubbles.

#### Bubble formation from an inclined surface

Not all membrane surfaces are horizontal flat planes. In tubular membranes and hollow-fiber membranes, the only small portion of membrane surface is in the horizontal position with respect to the field of the gravity. In a tilted surface, the buoyancy of the developing bubble creates the drifting force parallel to the membrane surface and changes the detachment mechanism, and consequently the size of emerging bubbles. Furthermore, bubbles often do not detach from an inclined surface, and merging of bubbles sliding on the inclined surface forms large bubbles.

In the bubble formation from a horizontal surface, the bubble development and the bubble detachment are coupled. When the buoyancy of a developing bubble overcomes the bubble attachment force due to the interfacial tension, the bubble detaches from the surface and completes the process of the bubble formation. A higher flow rate of air, in the low flow rate regime (e.g., 0.2–30 sccm), simply increases the frequency of the bubble formation but does not change the volume of bubble.<sup>1</sup>

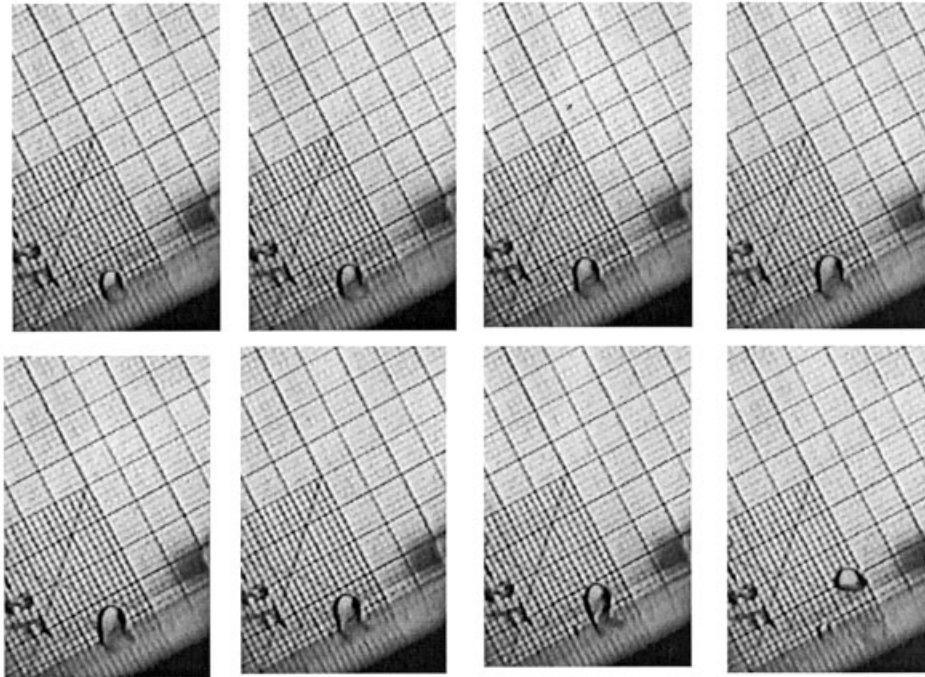
In the bubble formation from an inclined surface, however, the bubble development and the bubble detachment processes are decoupled, because a developing bubble could drift out of the orifice due to the component of the buoyancy parallel to the inclined surface. Once a sessile bubble drift out of the orifice,

the bubble development ceases, because no air is fed into a sliding bubble. Since the bubble development and detachment are decoupled, the flow rate of air becomes an important factor, which controls the frequency of sliding bubble formation. In other words, the drifting velocity of a drifted bubble and the surface velocity of the next bubble developing become important factors. A higher flow rate creates more number of sliding bubbles on an inclined surface.

#### Bubble detachment from the orifice (contact angle of water less than $45^\circ$ )

If the contact angle of water on the orifice surface is less than  $\pi/2$ , a developing bubble does not expand beyond the orifice, as discussed before. In this case, the tilting of the orifice surface does not change the basic bubble formation, and a bubble develops and detaches from the orifice. Figure 8, depicts sequentially captured bubble formation from an inclined surface with the tilt angle  $30^\circ$ . The effective cross-sectional area decreases with the tilt angle because a bubble develops along the line of the buoyancy, and the drifting force causes premature detachment of a developing bubble. Consequently, an inclined surface, in this domain, creates the bubble, which is smaller than the bubble emerging from a horizontal surface under otherwise identical conditions. The tilting angle has little influence in this domain (the effect of tilting angle is not shown).



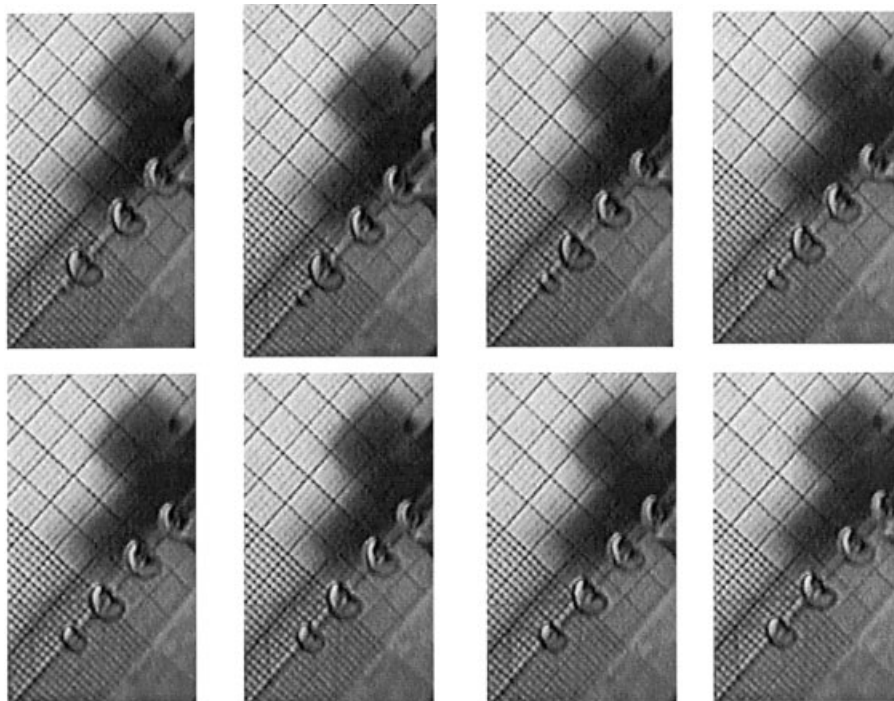


**Figure 9** Detachment of a bubble after a short slide on the surface: tilt angle  $30^\circ$ , contact angle of water  $82.7^\circ$ , orifice diameter 0.55 mm, air flow rate 4.36 mL/m, and bubble volume 0.047 mL/bubble.

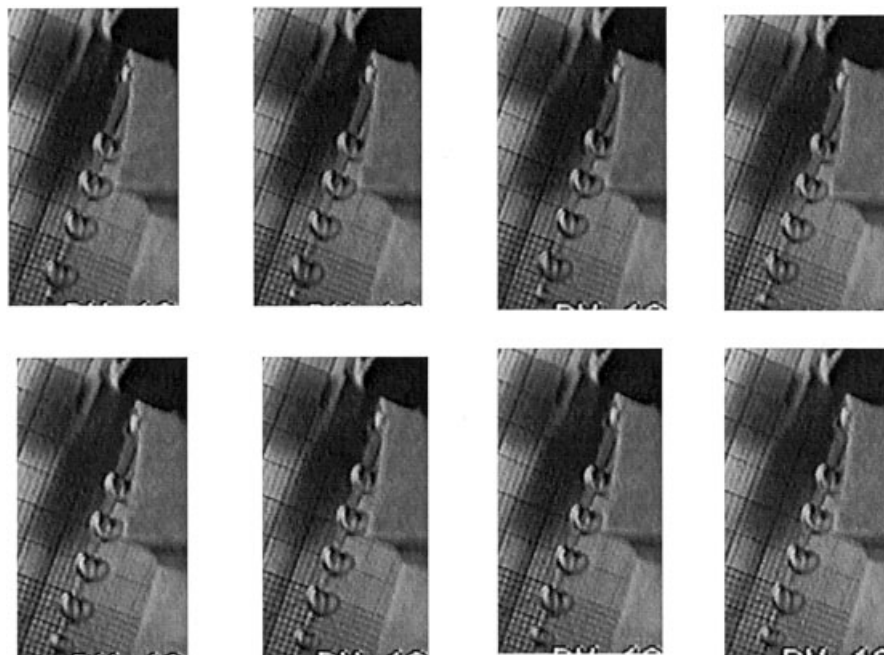
#### Detachment of drifted bubbles from the surface (contact angle of water greater than $45^\circ$ )

When a bubble drifts out of the orifice before its buoyancy increases to the critical level to detach the bubble

from the surface, the bubble slides on the surface. The detachment of the bubble can occur after the bubble slides for a short distance on the surface, as shown in Figure 9. If a bubble cannot detach from the surface



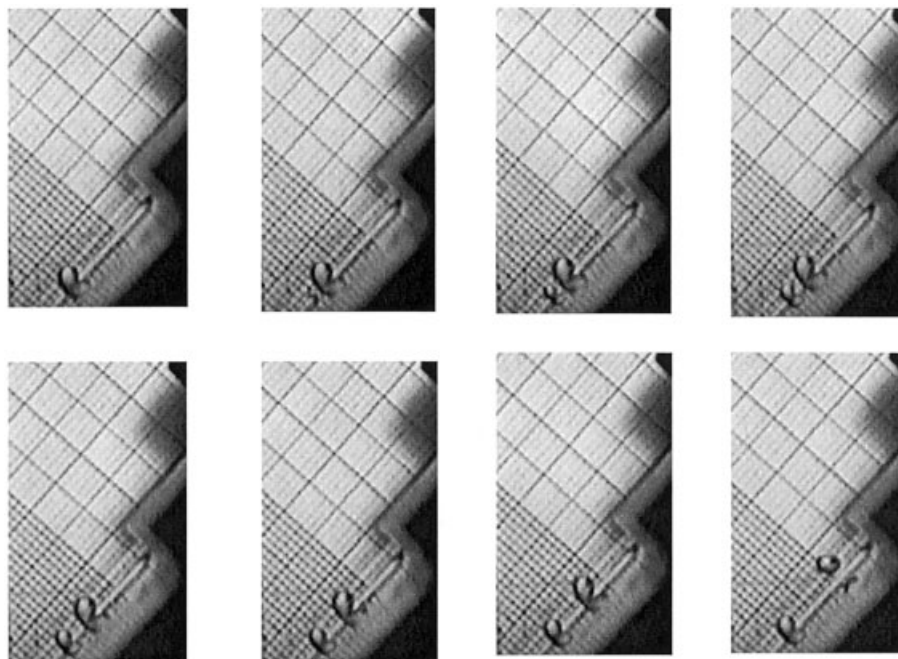
**Figure 10** No detachment occurs and bubbles slide on the surface: tilt angle  $45^\circ$ , contact angle of water  $82.7^\circ$ , orifice diameter 0.55 mm, air flow rate 4.36 mL/m, and bubble volume 0.047 mL/bubble.



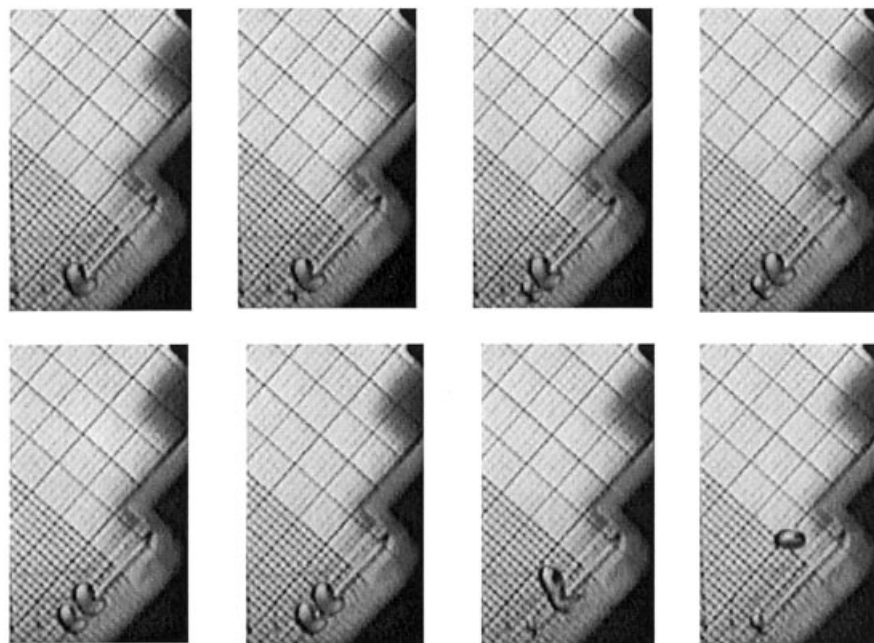
**Figure 11** No detachment occurs and bubbles slide on the surface: tilt angle  $60^\circ$ , contact angle of water  $82.7^\circ$ , orifice diameter 0.55 mm, air flow rate 1.73 mL/m, and bubble volume 0.047 mL/bubble.

within a short distance, the bubble keeps sliding on the surface until the bubble reaches to the end of surface and merges with the preceding or following bubble. The distance between two bubbles is determined by the sliding speed of a bubble on the surface

and the frequency of creating sliding bubbles, which is dependent on the flow rate of air. The sliding of bubbles occurs regardless of the tilt angle of plate as shown in Figure 10 (tilting angle  $45^\circ$ ) and Figure 11 (tilting angle  $60^\circ$ ).



**Figure 12** Effect of the flow rate on two drifted bubbles on the surface: tilt angle  $45^\circ$ , contact angle of water  $62.3^\circ$ , orifice diameter 0.55 mm, air flow rate 1.80 mL/m, and bubble volume 0.019 mL/bubble.



**Figure 13** Effect of the flow rate on two drifted bubbles on the surface; detachment of a bubble by emerging two sliding bubbles: tile angle  $45^\circ$ , contact angle of water  $62.3^\circ$ , orifice diameter 0.55 mm, air flow rate 4.76 mL/m, and bubble volume 0.024 mL/bubble.

#### A bubble detaches from the surface by merging two sliding bubbles

While the interfacial tension and the buoyancy of the bubble determine the sliding speed of an attached bubble, the frequency of creating a sliding bubble is determined by the flow rate of air. Figure 12 and Figure 13 show the influence of the flow rate of air on the detachment of sliding bubbles on the surface. In this case, numbers of sessile bubbles keep marching on maintaining a constant distance between them. Figure 12 depicts the case in which two adjacent sliding bubbles are separated due to the slow feeding of air. When the flow rate of air is increased, the second drifting bubble develops before the first bubble establishes the sliding on the tilted surface and bumps into the first bubble. When two bubbles merge together, the buoyancy of the merged bubble became sufficient to detach the bubble from the surface. Figure 13 depicts this case, in which the bubble volume is greater than corresponding bubble that emerges from a horizontal surface and also from the same inclined surface at lower flow rate.

#### IMPLICATIONS TO OXYGENATION MEMBRANE WITH MULTIPLE ORIFICIES

The fundamental factors of bubble formation and detachment carried out by using a single hole placed on a rigid stainless steel plate have important implications to small bubbles oxygenation membrane and eventually to the general gas-liquid reactions. The

main requirements for efficient small bubbles oxygenation membrane are (1) *small size hole*, and (2) *surface should be hydrophilic so that the contact angle of water is less than  $45^\circ$* . Implications of these fundamental requirements to membranes with multiple holes are as follows.

#### Density of holes on a surface

The diameter of a spherical bubble that detaches from the orifice is always greater than the diameter of the hole. If too many holes are created on a surface, the probability of merging of developing bubbles increases and it becomes difficult to create many small bubbles. The distance between two holes should be greater than the diameter of a spherical bubble that develops on membrane surface.

#### Horizontal surface is the best surface for small bubble formation

Tilted surface with multiple holes increases the probability of bubbles merging. Therefore, a flat horizontal surface is best to create many small bubbles. Creation of sliding bubbles should be avoided.

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