CHAPTER IV

RESULTS AND DISCUSSION
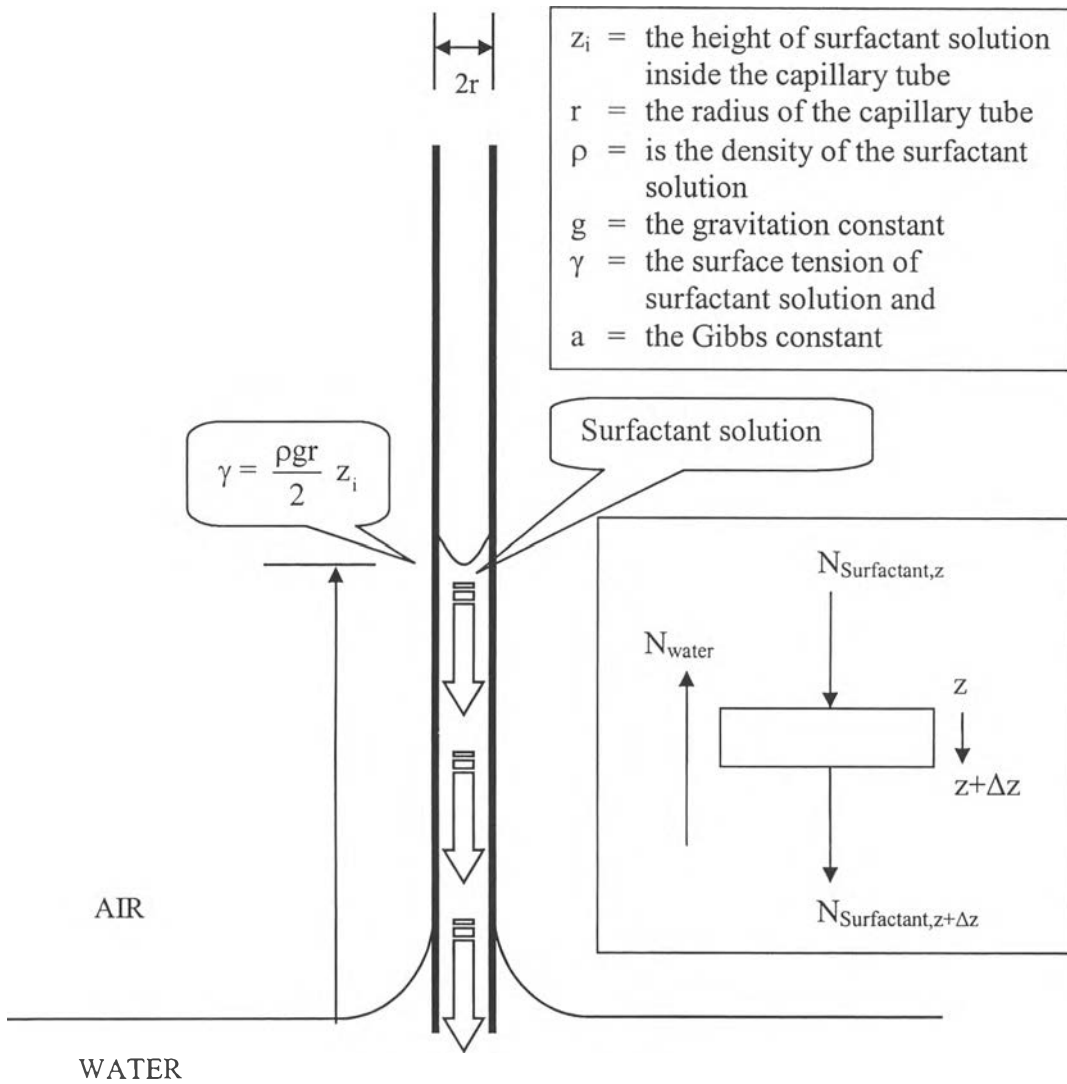
4.1 Mathematical Modeling

Figure 4.1 Schematic diagram of the transient capillary rise resulting from diffusion of a surfactant into water.

Figure 4.1 illustrates diffusion of a surfactant from a capillary tube into water. That results in a change of the surfactant solution height inside the tube.

The model was developed based on the theory of the capillary force, Gibbs plot (surface tension versus concentration), and mass transport of the surfactant in the tube. The mass transfer in the capillary tube can be written as shown in Equation 4.1

$$N_A = -C_0 \, D_{AB} \, \frac{\partial X_A}{\partial z} + X_A (N_A + N_B) \qquad (4.1)$$

Equation 4.1 then becomes

$$\frac{\partial X_A}{\partial z} - \frac{1}{D_{AB}} \left(\frac{\partial z_i}{\partial t} \right) X_A = -N_A \qquad (4.2)$$

Integrating Equation 4.2

$$X_A = \frac{N_A}{C_0 \left(\frac{\partial z_i}{\partial t} \right)} + C_i \exp \left[\frac{1}{D_{AB}} \left(\frac{\partial z_i}{\partial t} \right) z \right] \qquad (4.3)$$

where $z = 0$, $X_A = 0$, C_1 will be $- \dfrac{N_A}{C_0 \left(\frac{\partial z_i}{\partial t} \right)}$ and Equation 4.2 becomes

$$X_A = \frac{N_A}{C_0 \left(\frac{\partial z_i}{\partial t} \right)} \left(1 - \exp \left[\frac{1}{D_{AB}} \left(\frac{\partial z_i}{\partial t} \right) z \right] \right) \qquad (4.4)$$

At interface, $X_A = X_{A,i}$ and $z = z_i$ so Equation 4.4 becomes

$$X_{A,i} = \frac{N_A}{C_0 \left(\frac{\partial z_i}{\partial t} \right)} \left(1 - \exp \left[\frac{1}{D_{AB}} \left(\frac{\partial z_i}{\partial t} \right) z_i \right] \right) \qquad (4.5)$$

Note that $\frac{\partial z_i}{\partial t} < 0$ and $z_i < 0$ so the second term dominates the left hand side at short times. Equation 4.5 becomes

$$X_{A,i} = \frac{N_A}{C_0 \dfrac{z_i}{t}} \exp \frac{1}{D_{AB}} \frac{z_i}{t} z_i \qquad (4.6)$$

The Gibbs adsorption equation can be described as

$$\gamma = a \ln C + b \qquad (4.7)$$

The effect of capillary force can be accounted by

$$\gamma = \frac{rg\rho}{2} z_i \qquad (4.8)$$

Substitution of Equation 4.8 into Equation 4.7 gives

$$\frac{rg\rho}{2} z_i = a \ln C + b \qquad (4.9)$$

from $X_A = \dfrac{C}{C_0}$, Equations 4.9 becomes

$$X_A = \frac{1}{C_0} \exp \frac{-b}{a} .\exp \frac{\rho g r}{2} z_i \qquad (4.10)$$

Substitution of Equation 4.9 into Equation 4.6 gives

$$\frac{z_i}{t} = \frac{rg\rho D_{AB}}{2a} \qquad (4.10)$$

Note $\dfrac{z_i}{t} < 0$ and $z_i < 0$, integration of Equation 4.10 yields

$$z = z_0 - \frac{rg\rho D_{AB}}{2a} \left(t - t_0 \right) \qquad (4.11)$$

where t_0 is initial time, z_0 is initial height (mm), ρ is density if solution (kg/mm^3), g is gravitation constant (mm/s^2), r is radius of capillary (mm), and a Gibbs constant, (kg/s^2).

Equation 4.11 shows that the height of liquid inside the tube is a linear function with time, and diffusivity can be determined from the slope of the relationship between the height of liquid inside the tube and time.

Applying the model to previous data taken by Samuhavinyoo (2002), diffusivity of SDS at 1, 3, and 5 mM is consistent to those reported by Leaist and Abdu (2001) as shown in Table 4.1.

Table 4.1 Diffisivity from this model determined by using data from Samuhavinyoo (2002) compared to that from Leaist and Abdu (2001)[*].

Diffusivity Concentration (mM)	Transient Capillary Rise (cm^2/s)	Taylor Dispresion[*] (cm^2/s)	Leaist Model[*] (cm^2/s)
1.0	0.84±0.02	0.80	0.84
3.0	0.83±0.01	0.80	0.84
5.0	0.84±0.01	0.80	0.84

4.2 Effect of Capillary Size

Heights of SDS solution with initial concentration of 3 mM inside 1.16 and 0.34 mm ID tubes after flushing are shown in Figure 4.2.
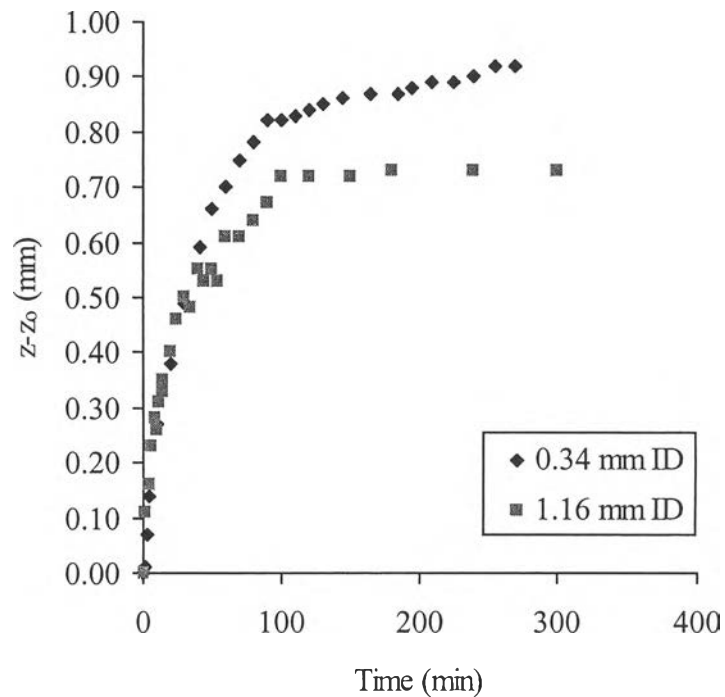
Figure 4.2 Effect of capillary size on the change in liquid height with time, initial SDS concentration of 3 mM, 0.34 mm ID (◆), 1.16 mm ID (■).

Figure 4.2 shows that the rate of the liquid height change in the 0.34 mm ID capillary tube is greater than that in the 1.16 mm ID capillary tube. Because diffusivity is independent on capillary radius, the rate of surface tension change is constant. From Equation 4.8, when the capillary ID is decreased, the rate of the liquid height change increases to maintain the rate of surface tension change.

The liquid height can be converted to surfactant concentration inside the tubes by using Equation 4.9. The results are shown in Figure 4.3.
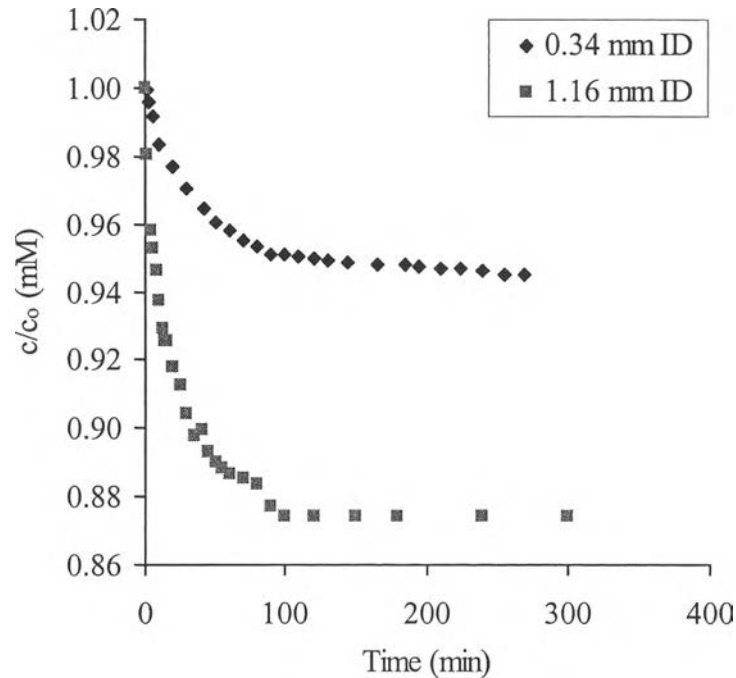
Figure 4.3 SDS concentration of surfactant solution inside the capillary tubes, initial SDS concentration of 3 mM, 0.34 mm ID (◆), 1.16 mm ID (■).

Figure 4.3 shows that the rate of concentration change in the 0.34 mm ID capillary tube is much less than that in the 1.16 mm ID capillary tube. Suppose that the experiment is to be taken at a low surfactant concentration (0.10 mM), only a small change (about 5% change) in the concentration in the 0.34 mm ID capillary tube can be observed. As a result, the rate of the liquid height change in the 0.34 mm ID capillary tube is too low and can not be measured as shown in Figure 4.4.
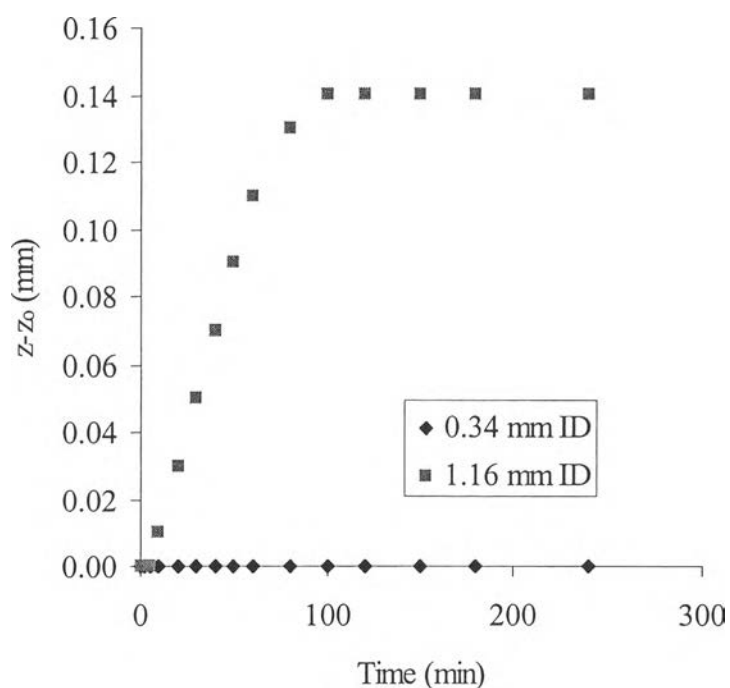
Figure 4.4 Effect of capillary size by the change in liquid height with time, initial SDS concentration of 0.25 mM SDS, 0.34 mm ID (♦), 1.16 mm ID (■).

From the previous discussion, it can be concluded that the 1.16 mm ID capillary tube is appropriate for carrying out the surfactant diffusivity measurements at low concentration or low CMC's surfactant.

4.3 Surface Tension Measurements

Surface tension of surfactant solutions at 25°C was also measured by the capillary tube method and Du-Nauy ring tensiometer. The Gibbs plot, the relationship between concentration and surface tension, was then created.

4.3.1 Surface Tension of SDS

The result of Surface tension of SDS solutions at 25°C are compared to those from Tsujii (1998) as shown in Figure 4.5.
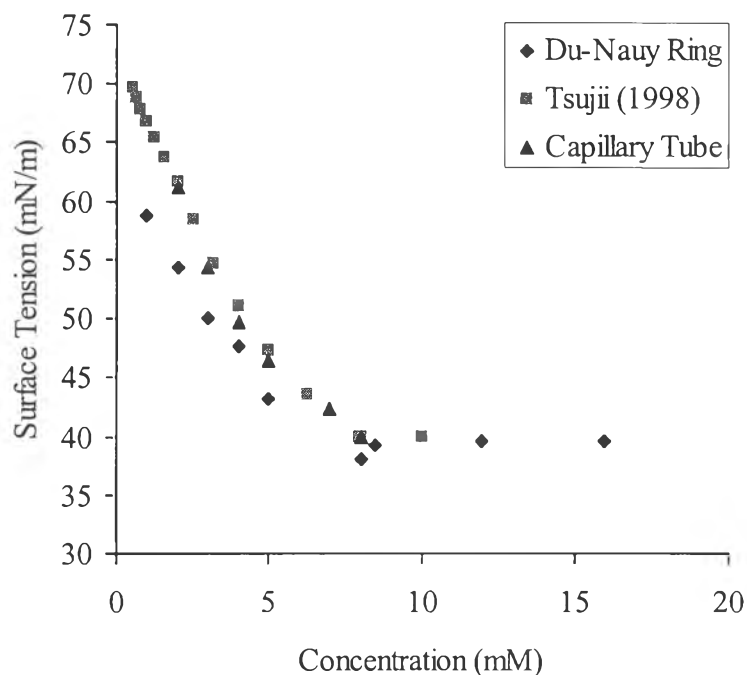

Figure 4.5 Comparison of the Gibbs plot from the capillary tube method (▲), Du-Nauy ring tensiometer (◆)and literature (Tsujii, 1998) (■) at 25 °C.

Figure 4.5 shows that the surface tension obtained from the capillary tube method is in good agreement with the results from Tsujii (1998) and Du-Nauy ring tensiometer. However, some discrepancies can be observed at low SDS concentration between the surface tension from the Du-Nauy ring tensiometer and the other two. The capillary tube method, once again, is validated as an alternative method that gives reliable results compared to the existing method and literature. Furthermore, CMC for the capillary tube method and Du-Nauy ring tensiometer are approximately 8 mM, compared to 8.2 mM reported by Rosen (1989).

4.3.2 Surface Tension of Triton X-100

Figure 4.6 shows the surface tension of Triton X-100 solutions at 25°C and the CMC of Triton X-100 from the Du-Nauy Ring tensiometer is 0.28 mM and the capillary tube method, 0.28 mM, compared to 0.30 mM reported by Rosen (1989). The surface tension obtained from the capillary tube method is higher than the Du-Nauy ring tensiometer.
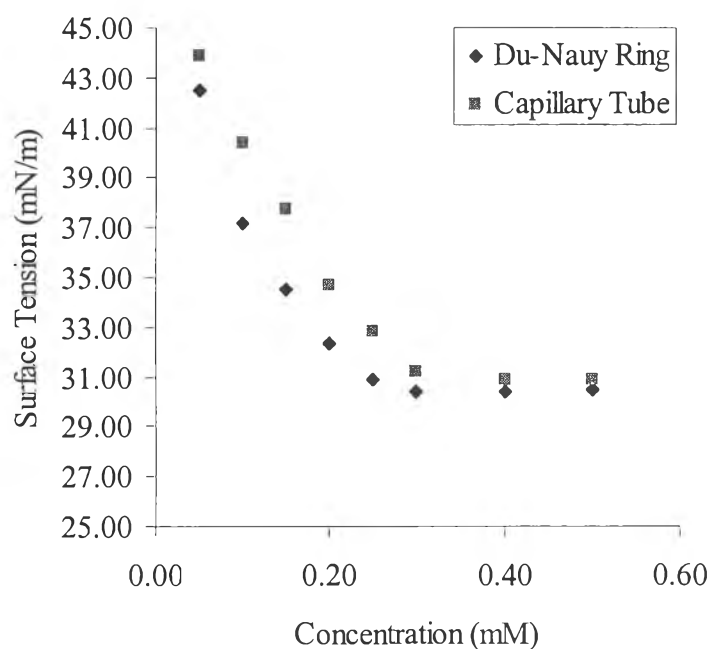

Figure 4.6 Relationship between surface tension and concentration of Triton X-100, determined by Du-Nauy Ring tensiometer (◆) and the capillary method (■).

4.3.3 Surface Tension of CTAB

Surface tension of CTAB solutions at 25°C is shown in Figure 4.7 and the result shows that the CMC of CTAB from the Du-Nauy Ring tensiometer is 0.90 mM, compared to 0.92 mM reported by Rosen (1989) but CMC from the capillary tube method is less than 0.01 mM because of the point of zero charge (PZC) of the tube. As the tube is made of silica with PZC between 2-3, with deionized water with pH about 6, silica surface is negativly charged so CTAB may adsorb on the capillary tube and form monolayer coverage because CTAB monomer that required for adsorption (1.4449×10^{-11} mole) is much lower than CTAB monomer in the capillary

tube (1.2808×10^{-10} mole). As a result of the monolayer coverage, the surface tension of CTAB is constant because the amount of monomer adsorption can reduce surface tension and at its equilibrium, monolayer coverage, the surface tension is constant; therefore CMC of CTAB that determined by the capillary tube method is less than 0.01 mM (Rosen 1989).

This method is not suitable for the CTAB diffusivity measurements because surface tension form the capillary tube method tends to be constant at any concentration.
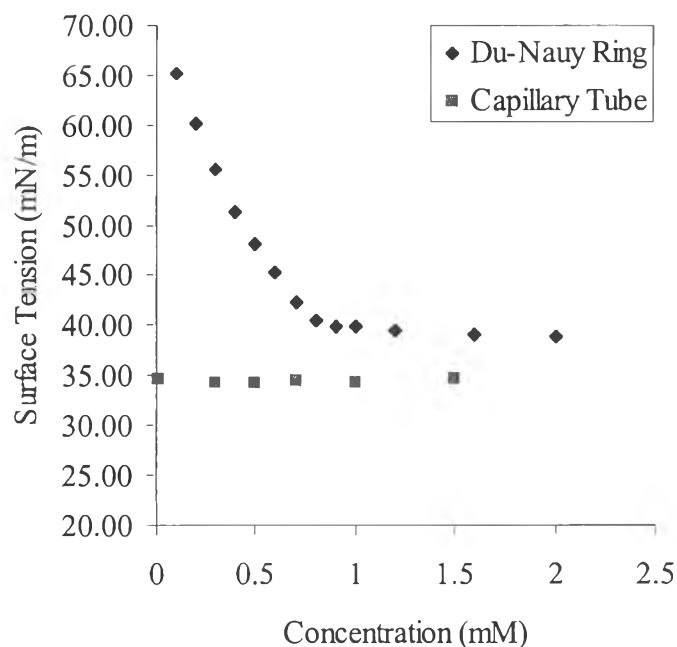

Figure 4.7 Relationship between surface tension and concentration of CTAB, determined by Du-Nauy Ring tensiometer (◆) and the capillary method (■).

4.4 Diffusivity Determination

In the trainsient capillary rise method, after flushing the surfactant solution with water, height of surfactant solution inside the capillary tube changes as a result of the surfactant diffusion from the tube. Experimentally, the change of the height was monitored as a function of time. To determine surfactant diffusivity, a mass transport model has been developed as described previously.

4.4.1 SDS Diffusivity

The height of SDS solution inside the capillary tube with 1.16 mm ID after flushing is shown in Figure 4.8.

From the transient capillary rise results of the SDS solutions in Figure 4.8 show that the effect of flushing causes the increase in the bulk liquid level in the beaker. As a result, the height of SDS solution inside the capillary tube increases rapidly during the first period, about 5 to 8 min. It, however, does not affect the diffusion of the surfactant. That is because, after this period, the diffusion process takes place, the height of the liquid inside the tube increases resulted from the decrease in the surfactant solution in the tube, which is caused by the diffusion of surfactant from the tube to the bulk liquid in the beaker. The new mass transport model is fitted in this period as shown in Figure 4.9. After that, the third period, the height of SDS solution inside the capillary tube tends to be constant.

Note that the starting liquid heights of each concentration in Figure 4.8 are different. That is resulted from different surface tension of different surfactant concentration.

Figure 4.9 shows the determination of SDS diffusivity using the linear least square method. Diffusivity was determined from the slope using Equation 4.11. Diffisivity of SDS from this model is about 8.40×10^{-6} cm^2/s. This value is close to those from the Taylor Dispersion method (8.00×10^{-6} cm^2/s) and Leaist model (8.40×10^{-6} cm^2/s) as shown in Table 4.2.
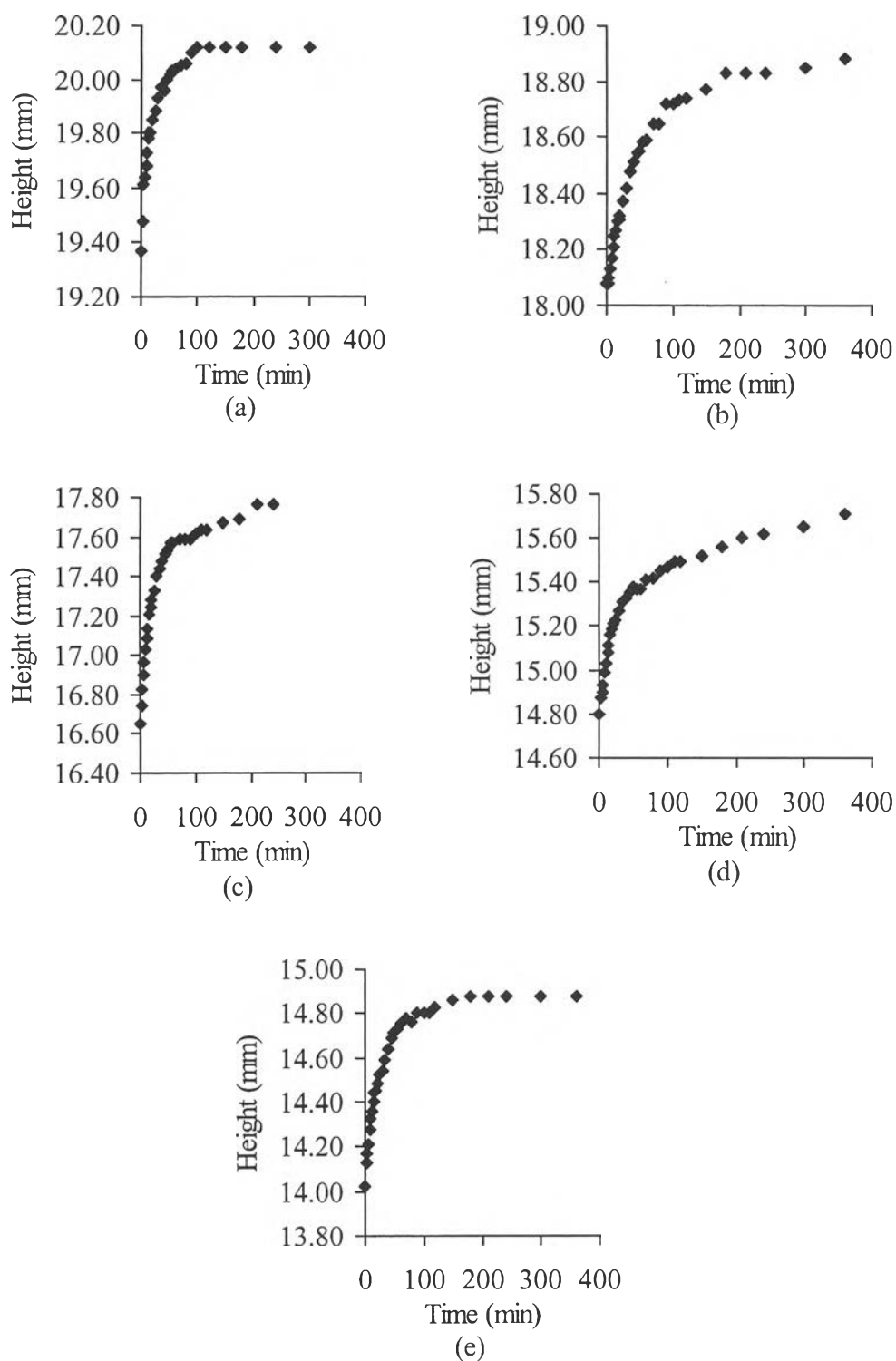
Figure 4.8 Height of SDS solution inside the capillary tube with 1.16 mmID after flushing (a) 3 mM, (b) 4 mM, (c) 5 mM, (d) 7 mM, and (e) 8 mM
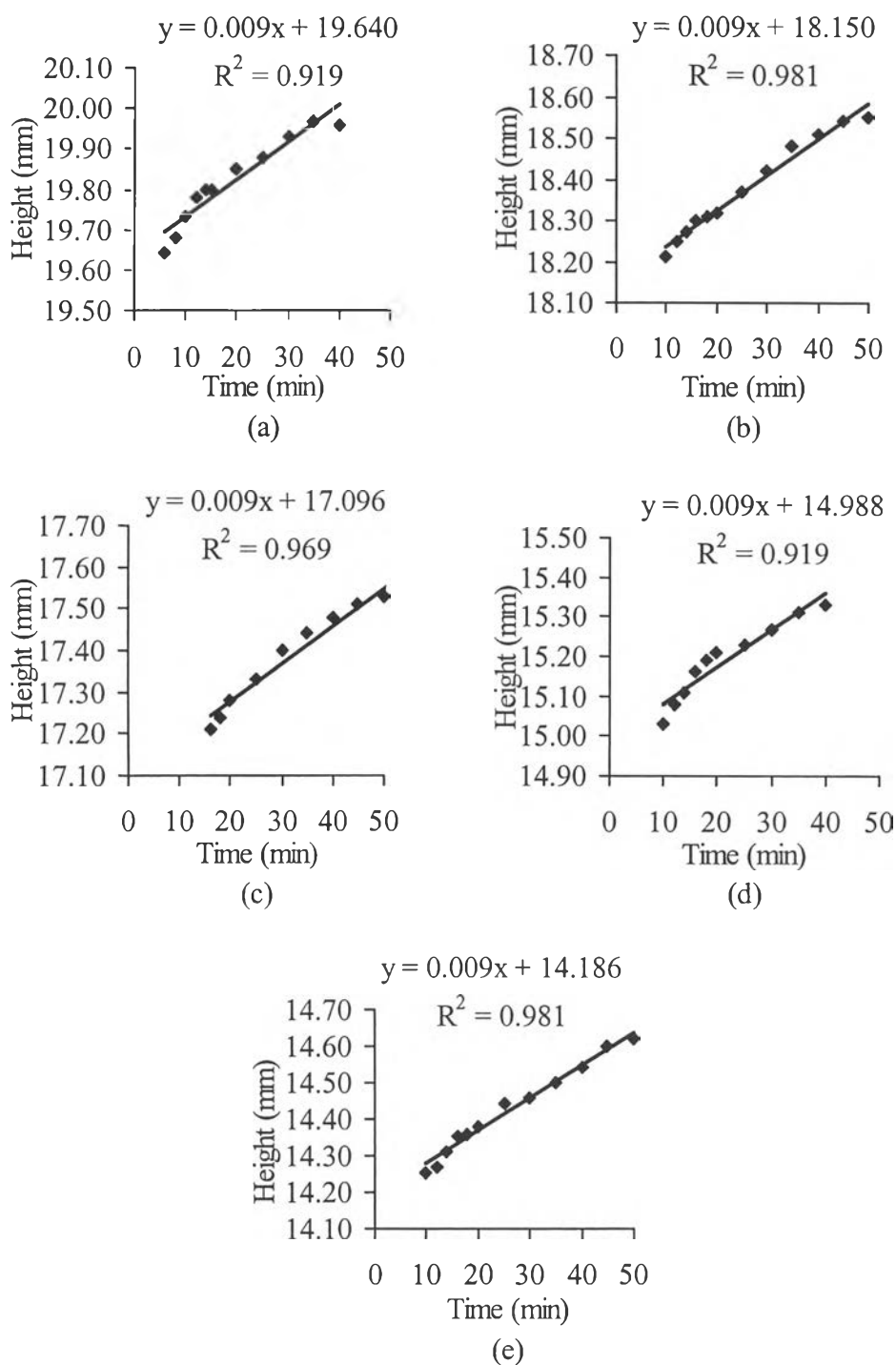
Figure 4.9 Slope determination of SDS results using linear least square method (a) 3 mM, (b) 4 mM, (c) 5 mM, (d) 7 mM, and (e) 8 mM

Table 4.2 Diffusivity of SDS from this model compared to that from the Taylor dispersion method and Leaist model.

Diffusivity Concentration (mM)	Transient Capillary Rise $D \times 10^6$ (cm²/s)	Taylor Dispersion $D \times 10^6$ (cm²/s)	Leaist Model $D \times 10^6$ (cm²/s)
3.0	8.42±0.15	8.00	8.40
4.0	8.34±0.11	8.00	8.40
5.0	8.46±0.14	8.00	8.40
7.0	8.30±0.17	8.00	8.40
8.0	8.37±0.12	8.00	8.40

4.4.2 Triton X-100 Diffusivity

Figure 4.10 shows the height of Triton X-100 solution inside the 1.16 mm ID capillary tube after flushing. The trend is the same with the SDS result such as the effect of flushing in the frist period, diffusion process takes place in the second period, and reaching equibrium after 120 min. Note that because of the result from different surface tension of different surfactant concentration, the starting liquid heights of each concentration in Figure 4.10 are different.

The determination of Triton X-100 diffusivity is shown in Figure 4.11 by using the linear least square method. Diffusivity was determined from the slope using Equation 4.11. Diffisivity of Triton X-100 from this model is about 7.80×10^{-7} cm²/s. This value is close to those from the Taylor Dispersion method (8.25×10^{-6} cm²/s) as shown in Table 4.3.
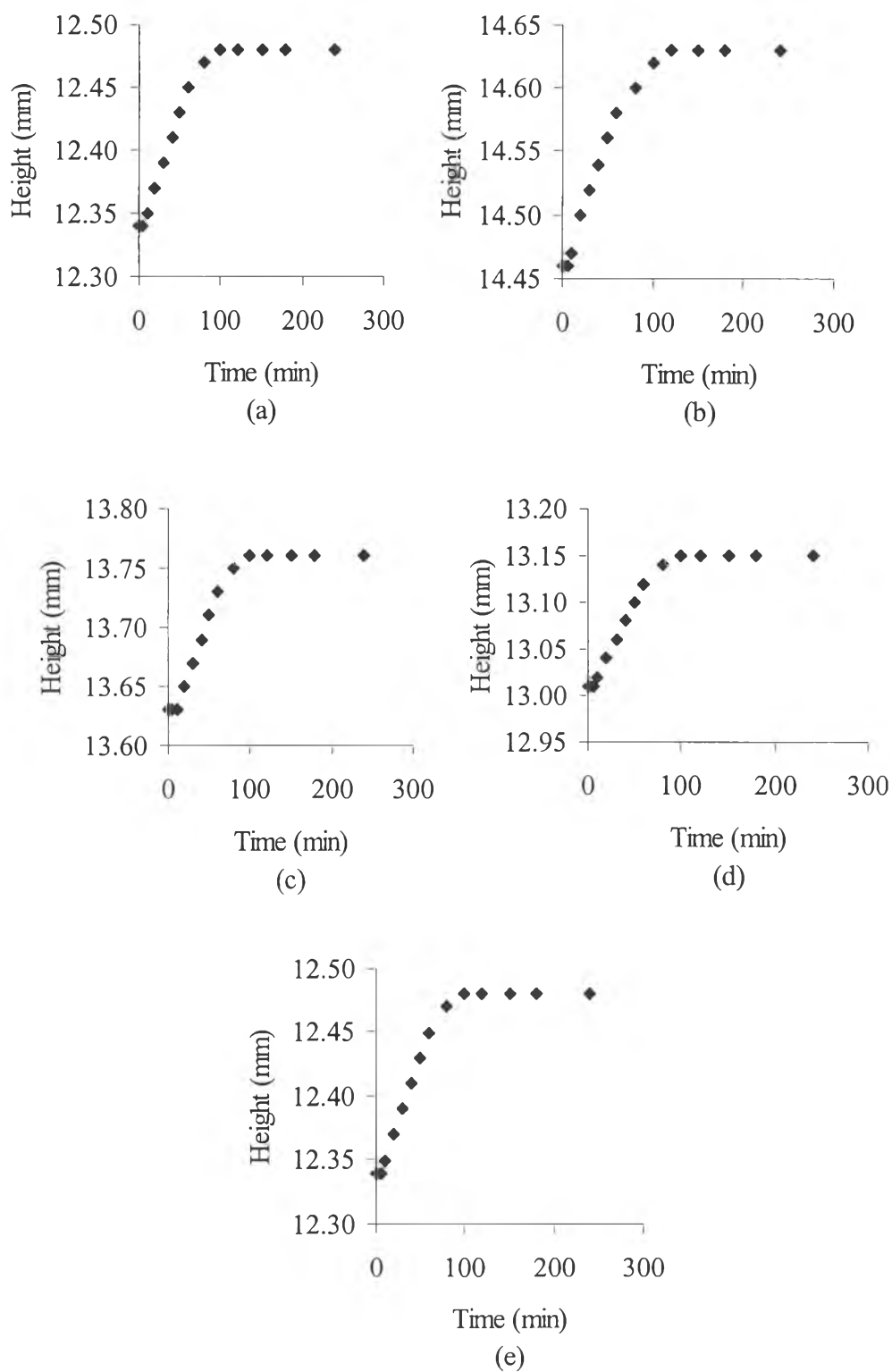
Figure 4.10 Height of Triton X-100 solution inside the capillary tube with 1.16 mm ID after flushing (a) 0.05 mM, (b) 0.10 mM, (c) 0.15 mM, (d) 0.20 mM, and (e) 0.25 mM
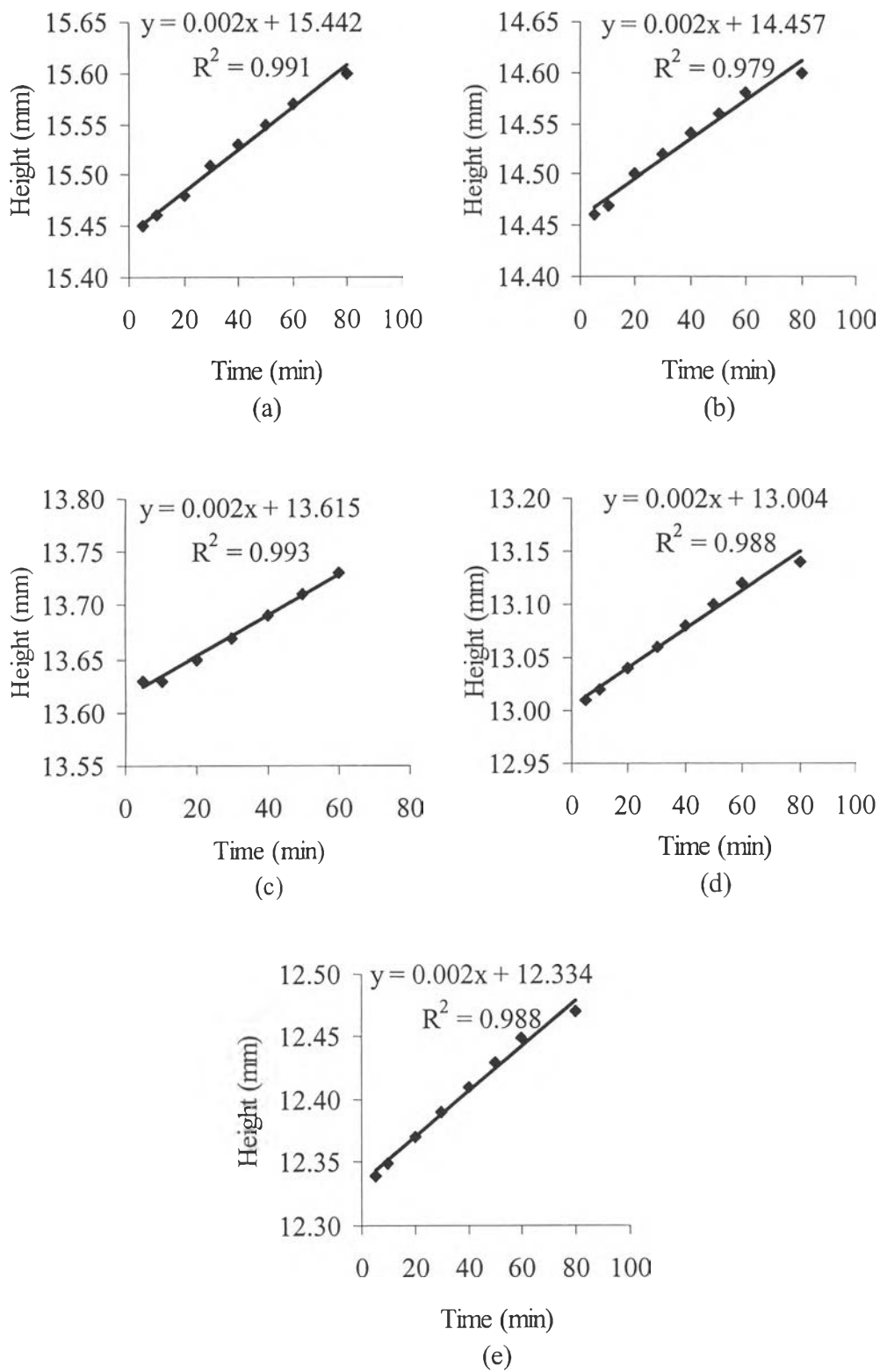
Figure 4.11 Slope determination of Triton X-100 results using linear least square method (a) 0.05 mM, (b) 0.10 mM, (c) 0.15 mM, (d) 0.20 mM, and (e) 0.25 mM

Table 4.3 Diffusivity of Triton X-100 from this model compared to that from the Taylor dispersion method and Leaist model.

Diffusivity Concentration (mM)	Transient Capillary Rise $D \times 10^7$ (cm^2/s)	Taylor Dispersion $D \times 10^7$ (cm^2/s)
0.05	7.87±0.43	8.25
0.10	7.98±0.34	8.25
0.15	7.58±0.31	8.25
0.20	7.49±0.21	8.25
0.25	7.47±0.19	8.25