CHAPTER IV
RESULTS AND DISCUSSION

4.1 Surface Tension Measurements

4.1.1 Surface Tension of Deionized Distilled Water

Surface tension of deionized distilled water measured by the capillary tube and Du-Nauy ring tensiometer compared with the literature value at 25 °C is shown in Table 4.1.

Table 4.1 Surface tension of deionized distilled water at 25 °C

Method	Surface Tension (mN/m)
Capillary Tube	70.58±0.20
Du-Nuoy Ring Tensiometer	72.95±0.05
Literature (Kruss, 1992)	71.50

The result shows that the surface tension from the capillary tube method is in good agreement with those from the Du-Nauy ring tensiometer and literature. The deviation is less than 1.2 mN/m. This assures the validity of the experimental set-up and procedure for the surface tension measurement.

4.1.2 Surface Tension of SDS

Surface tension of SDS solutions at 25 °C was also measured by the capillary tube and Du-Nauy ring tensiometer. The Gibbs plot, the relationship between concentration and surface tension, was then created. The result is compared to those from Tsujii (1998) as shown in Figure 4.1.
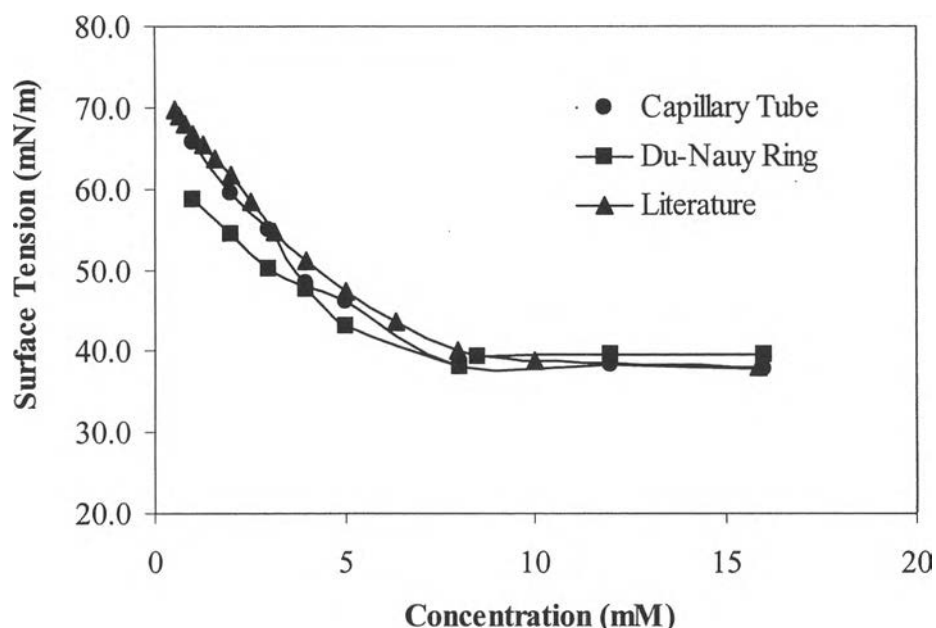
Figure 4.1 Comparison of the Gibbs plot from the capillary tube method, Du-Nauy ring tensiometer and literature (Tsujii, 1998) at 25 °C.

The result 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 were 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 alternate practical 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).

4.2 Model Development

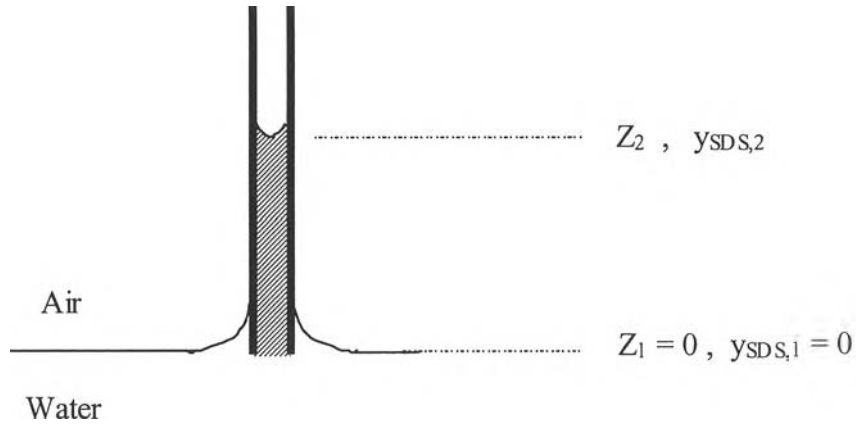The schematic diagram of the transient capillary rise system is shown in Figure 4.2.

Figure 4.2 The schematic diagram of the transient capillary rise system.

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 easily taken care by equation (2.5). The equation can then be simplified to

$$N_{SDS,Z} = -CD_{SDS/H_2O}\frac{dy_{SDS}}{dZ} + y_{SDS}\left(N_{SDS,Z} + N_{H_2O,Z}\right) \qquad (4.1)$$

with the following assumption:

1.) No bulk liquid motion inside the capillary tube
2.) Very small concentration of SDS
3.) A small change in the meniscus height inside the tube (Pseudo steady state)
4.) An insignificant change in the surfactant solution concentration at the meniscus over a long period of time

The second term in the RHS of equation (4.1) is dropped out due to no bulk liquid motion and very small y_{SDS}. The equation is reduced to

$$N_{SDS,Z}dZ = -CD_{SDS/H_2O}dy_{SDS} \qquad (4.2)$$

Integrating both sides of equation (4.2) yields

$$N_{SDS,z}(Z_2 - Z_1) = -CD_{SDS/H_2O}(y_{SDS,2} - y_{SDS,1}) \qquad (4.3)$$

where

$y_{SDS,1}$ = mole fraction of SDS at the bottom of liquid inside the tube

$y_{SDS,2}$ = mole fraction of SDS at the meniscus of liquid inside the tube

Z_1 = reference height ($Z_1 = 0$)

Z_2 = the height of liquid inside the tube

Boundary condition: at $t \geq 0$, $y_{SDS,1} = 0$ $\qquad (4.4)$

From the pseudo steady state assumption, the height is constant over a long period of time ($Z_2 - Z_1 = Z$), where $y_{SDS,1} = 0$. Then, equation (4.3) becomes

$$N_{SDS,z} = \frac{-CD_{SDS/H_2O}\,y_{SDS,2}}{Z} \qquad (4.5)$$

The effect of capillary force can be accounted by

$$\gamma = \frac{rg\rho}{2}h \qquad (2.1)$$

Differentiating both sides with respect to time gives

$$\frac{d\gamma}{dt} = \frac{rg\rho}{2}\frac{dh}{dt} \qquad (4.6)$$

According to the Gibbs plot (Figure 4.1), the surface tension below CMC can be correlated with

$$\gamma = aC_{SDS} + b \tag{4.7}$$

Where a and b are constants and can be obtained from the experimental data. The values of a and b for this work are -5.12 kg.l/mol.s^2 and 71.84 mN/m. Details are in Appendix A. Then, substitute equation (4.7) into equation (4.6)

$$\frac{a\left(aC_{SDS} + b\right)}{dt} = \frac{rg\rho}{2}\frac{dZ}{dt} \tag{4.8}$$

$$\frac{dC_{SDS}}{dt} = \frac{rg\rho}{2a}\frac{dZ}{dt} \tag{4.9}$$

Multiplied both sides by Z,

$$Z\frac{dC_{SDS}}{dt} = \frac{rg\rho}{2a}Z\frac{dZ}{dt} \tag{4.10}$$

The LHS is the definition of the molar flux, then the equation (4.10) can be rewritten to

$$N_{SDS,Z} = \frac{rg\rho}{2a}Z\frac{dZ}{dt} \tag{4.11}$$

By equating equation (4.5) to equation (4.11), the relationship between the liquid height inside the tube and time can be obtained

$$Z^2 dZ = \frac{-2aCD_{SDS/H_2O}\,y_{SDS,2}}{rg\rho}dt \tag{4.12}$$

From the assumption that the concentration of SDS solution at the meniscus hardly changes over a long period of time, then $y_{SDS,2}$ is constant. Integration of equation (4.12) becomes

$$Z_t^3 - Z_{t_0}^3 = \frac{-6aCD_{SDS/H_2O}\, y_{SDS,2}}{rg\rho}(t - t_0) \qquad (4.13)$$

where t =   the observed time

t_0 =   the starting time

Z_t =   the liquid height at time t

Z_{t0} =   the liquid height at starting time

4.3 Transient Capillary Rise Measurements

The results of the transient capillary rise of SDS solutions at 1, 2, 3, 4, 5, 12 and 16 mM at 25 °C are shown in Figures 4.3 - 4.9. The figures show the change of the liquid height inside the capillary tube as a function of time after the SDS solution was flushed out. Each experiment was carried out at least 3 times. It is represented in the figures with different legends. The experimental data has low standard deviations with the maximum value of 0.4 mm. As a result, the experiment can be reproduced with a high degree of accuracy.

From the results, it can be seen that the effect of flushing causes the increase in the bulk liquid level in the beaker. As a result, the height of the liquid inside the capillary tube increases rapidly during the first period. It, however, does not affect the diffusion of the surfactant. That is because, in the later period, when the diffusion takes place, the height of the liquid inside the tube increases for the concentrations below CMC (Figures 4.3 - 4.7) and remains constant for the concentrations above CMC (Figures 4.8 - 4.9).
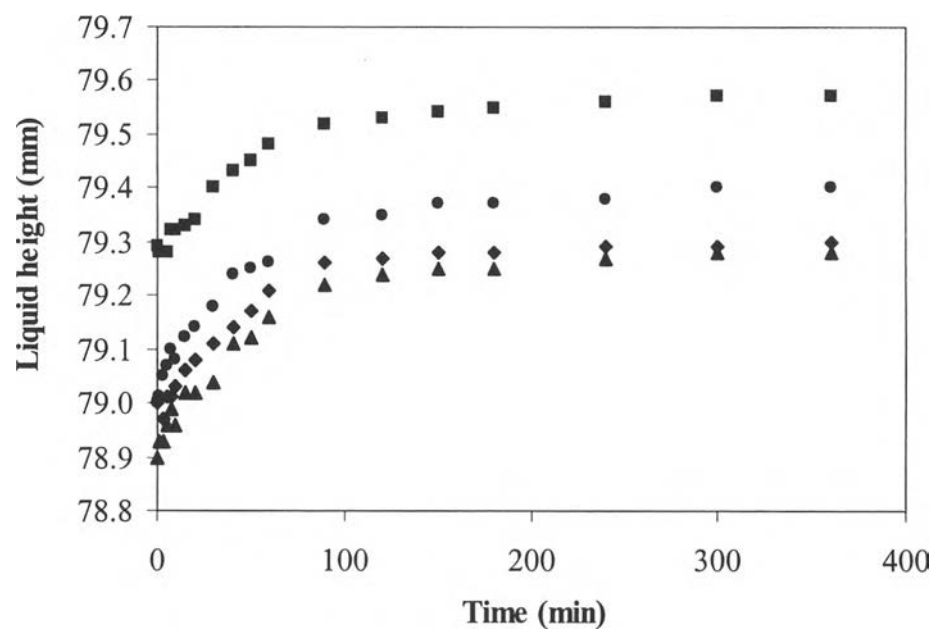
Figure 4.3 The transient capillary rise of SDS at concentration 1 mM.
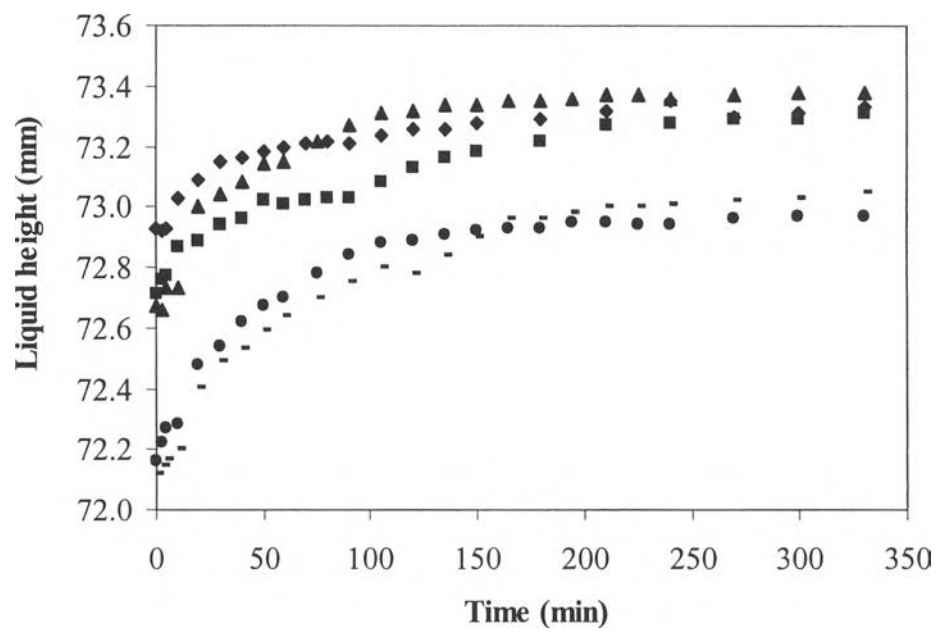

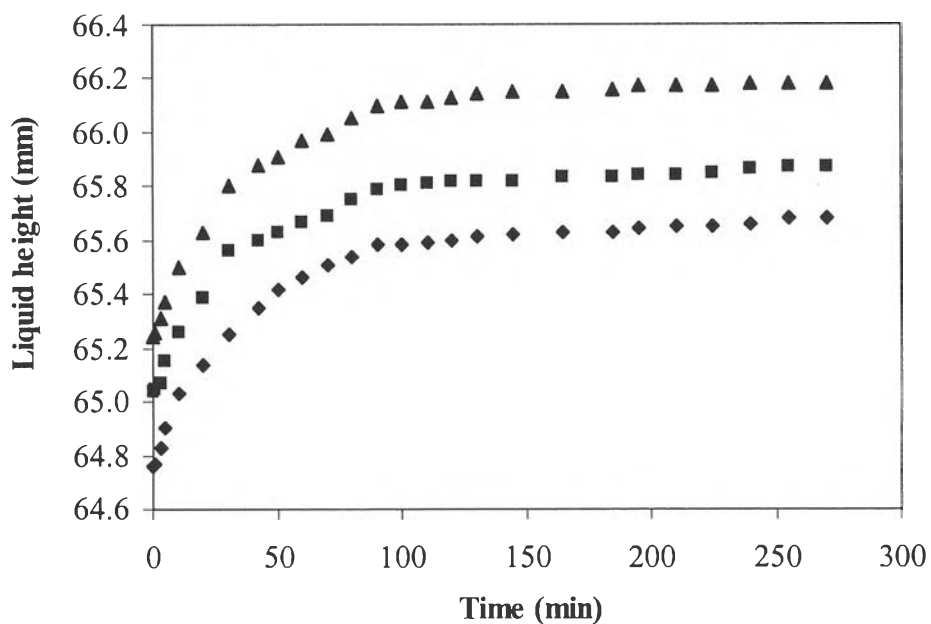**Figure 4.4** The transient capillary rise of SDS at concentration 2 mM

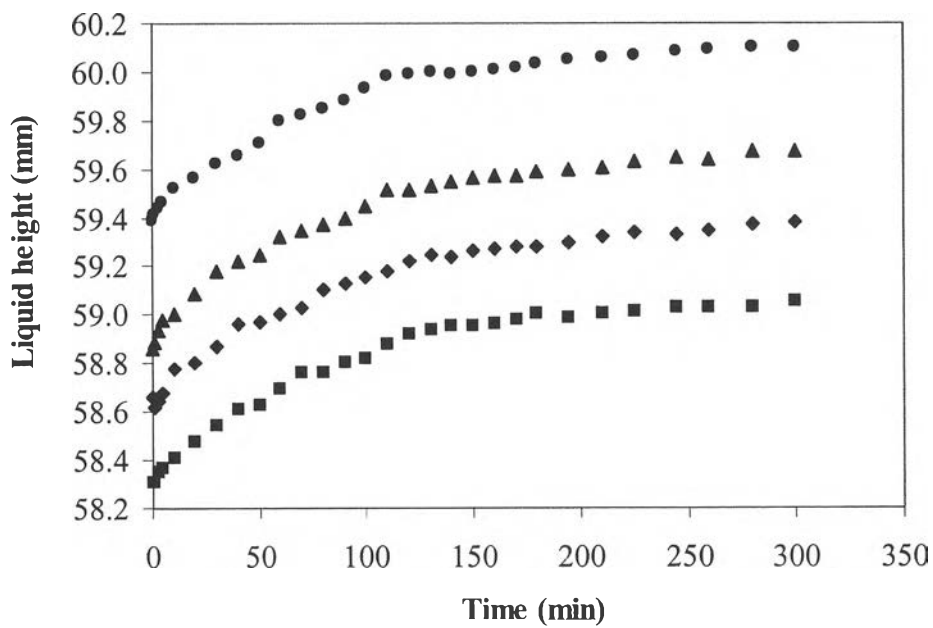Figure 4.5 The transient capillary rise of SDS at concentration 3 mM

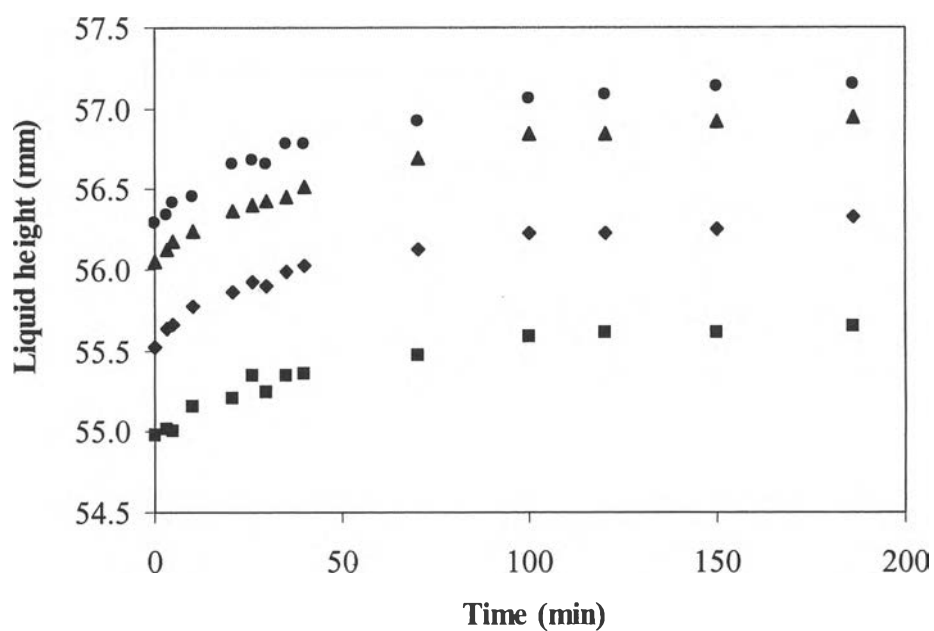Figure 4.6 The transient capillary rise of SDS at concentration 4 mM

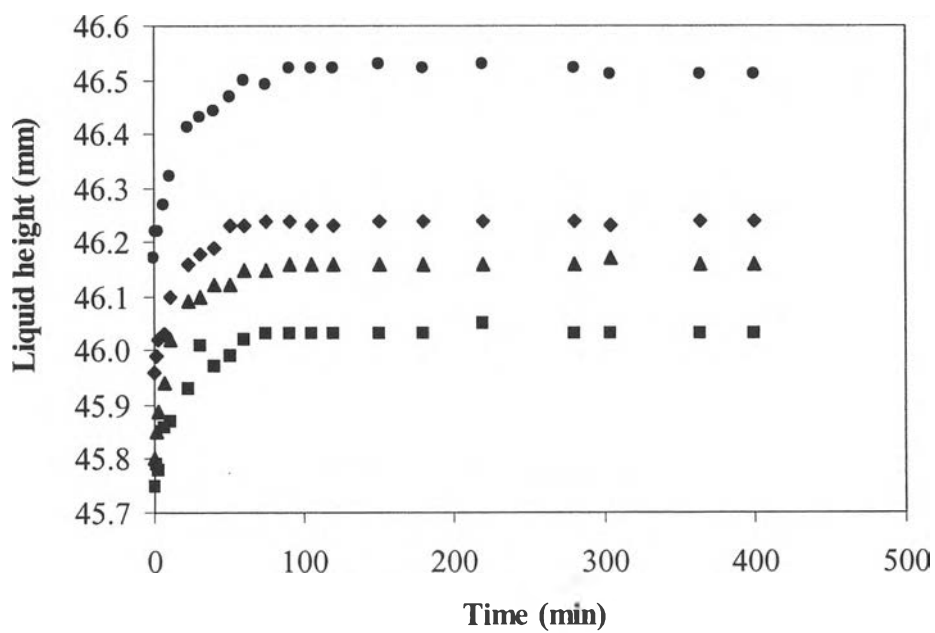**Figure 4.7** The transient capillary rise of SDS at concentration 5 mM

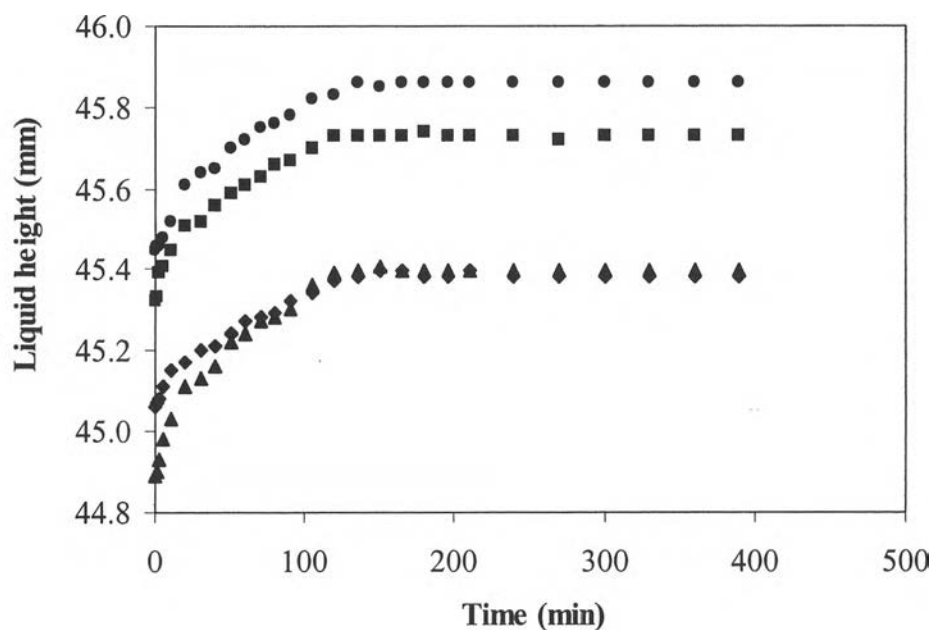**Figure 4.8** The transient capillary rise of SDS at concentration 12 mM

Figure 4.9 The transient capillary rise of SDS at concentration 16 mM

As implied in Figure 4.1, the surface tension of the liquid inside the capillary tube changes inversely with the concentration of SDS solutions where the concentration is below CMC and remains constant over a concentration above CMC. The transient capillary rise method may not be suitable for the diffusivity determination when the surfactant concentration is higher than CMC because of the time requirement.

Equation (4.13) was used to fit the experimental data (Figures 4.3 – 4.7) to obtain the SDS diffusivity at 1, 2, 3, 4, and 5 mM. Details are shown in Appendix B. The diffusivity from this work was compared to those from the Taylor dispersion method (Evan, 1983) and Leaist analytical equation (equation (2.7)). The comparison is shown in Table 4.2.

Table 4.2 Diffusivity of SDS

Concentration (mM)	SDS Diffusivity (10^{-5} cm^2/s)		
	Transient Capillary Rise	Leaist Model (Leaist, 2001)	Taylor Dispersion (Evan, 1983)
1	3.93±0.83	0.84	-
2	2.62±1.16	0.84	0.79
3	2.07±0.21	0.84	0.78
4	1.88±0.29	0.84	0.77
5	1.74±0.34	0.84	0.77

The SDS diffusivity in water for this work is in the range of 1.74×10^{-5} to 3.93×10^{-5} cm^2/s over 1 to 5 mM of SDS. However, the Leaist model and results from Evan (1983) show an approximately constant value of SDS diffusivity, 0.84×10^{-5} and 0.78×10^{-5} cm^2/s. Even though the results obtained from this work are higher than those from the other two sources, more experimental data of SDS diffusivity from another method is needed.