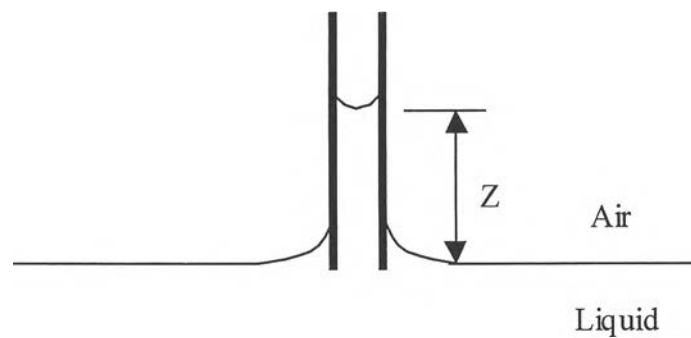




## CHAPTER II LITERATURE SURVEY

### 2.1 Capillarity Theory

One of the most classical methods for determining surface tension of liquid is based on the capillary force in a capillary tube. The schematic diagram of the capillary method is shown in Figure 2.1.



**Figure 2.1** The schematic diagram of the capillary method.

Cutler *et al.* (1975) stated that the height to which a liquid in a capillary will rise depends on the radius of the tube, the surface tension of the liquid, the density of the liquid, and the contact angle between the tube wall, the air, and the liquid. The equation that provides an adequate treatment of the phenomenon is

$$\gamma = \frac{gr\rho}{2} Z \quad (2.1)$$

- where  $\gamma$  = the surface tension of the liquid  
 $g$  = the gravitation constant  
 $r$  = the radius of the capillary tube  
 $\rho$  = the density of the test liquid  
 $Z$  = the height of the liquid rise in the capillary tube

This equation is applicable if the liquid completely wets the walls of the capillary tube, giving a contact angle of zero. If the contact angle  $\theta$  is not  $0^\circ$  or  $180^\circ$ , then the expression is

$$\gamma \cos \theta = \frac{gr\rho}{2} Z \quad (2.2)$$

The general attributes of the capillary method were summarized by Adamson (1976). This method is considered to be one of the most accurate absolute methods and good to a few hundredths of a percent in precision. On the other hand, for practical reasons, a zero contact angle is required and fairly large volumes of solution are needed. A number of variations in the capillary rise method have been developed for ultimate accuracy, it is necessary to obtain capillaries with a uniform radius. This can be avoided if the meniscus can always be brought to the same point. This may be done by rising or lowering the outer liquid level until the meniscus stands at the reference point.

## 2.2 Molecular Mass Transfer Theory

The theory of molecular mass transfer was dated back a long time. This phenomenon was first observed by Parrot (1815). He observed qualitatively that whenever a gas mixture contains two or more molecular species, whose relative concentrations vary from point to point, an apparently natural process results which tends to minimizing the concentration differences within the system. The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

Later, Bird *et al.* (1960) indicated that diffusion of A in a binary system of A and B occurs because of a concentration gradient of A which is called ordinary diffusion. However, there are a number of other physical conditions, in addition to the difference in concentration, which produces a chemical potential gradient: temperature differences, pressure differences and differences in the forced created by external field, such as gravity, magnetic and electrical fields. For example, mass

transfer obtained by applying a temperature gradient to a multicomponent system, component in a liquid mixture can be separated with a centrifuge by pressure diffusion and mineral mixture separated through the action of a magnetic force field.

Welty *et al.* (1984) stated the definition of a vector quantity denoting the amount of the particular species in molar units that passes per given increment of time through a unit area normal to the vector is called the molar flux. They also reviewed the Fick's law of mass transfer that shows the relation between the flux of the diffusing substance and the concentration gradient responsible for this mass transfer. The relations of the total molar flux of component A in z direction is shown in equation (2.3).

$$N_A = -CD_{AB}\nabla x_A + x_A(N_A + N_B) \quad (2.3)$$

where  $N_A$  = the total molar flux of component A in z direction  
 $N_B$  = the total molar flux of component B in z direction  
 $C$  = the bulk concentration of mixture  
 $D_{AB}$  = the diffusion coefficient for component A diffusing through component B  
 $x_A$  = the mole fraction of component A

From equation (2.3), the molar flux,  $N_A$ , is a result of the two vector quantities. The first term resulting from the concentration gradient is referred to as the concentration gradient contribution whereas the other term resulting as component A is carried in the bulk flow of the fluid. This flux term is designated the bulk motion contribution.

### 2.3 Taylor Dispersion Method

Pratt and Wakeham (1974) introduced the Taylor dispersion (peak-broadening) method in order to measure the mutual diffusion coefficients of the solutions. In this method, a small sample (20  $\mu$ l) is injected into a carrier stream as it

flows through a capillary tube. Provided the flow is laminar, the combination of the flow and diffusion results in the Gaussian distribution of the solute with respect to the axial position along the tube. Experimentally, it is more convenient to measure the variation in concentration with time at a fixed location. The resulting concentration profile is given as shown in equation (2.4).

$$\frac{c - \bar{c}}{c_{max}} = \left(\frac{t_R}{t}\right)^{1/2} \exp\left[-12D \frac{(t - t_R)^2}{r^2 t}\right] \quad (2.4)$$

where  $D$  = the effective diffusion coefficient

$r$  = the radius of the tube

$\bar{c}$  = the average surfactant concentration without the pulse

$c$  = the surfactant concentration averaged across the tube radius at time  $t$

$c_{max}$  = the maximum value of  $c$

$t_R$  = the residence time (the tube length divided by the average solution velocity)

$t$  = time

The diffusion coefficient is obtained by nonlinear least-square fit of the observed concentration profile.

Leaist *et al.* (1986) proposed an alternative to monitor the broadened distribution of the injected sample at the outlet of a long capillary tube by a liquid-chromatography differential refractometer detector. Surfactant diffusivity can be calculated from the least-square fit of the dispersion equation as shown in equation (2.5).

$$V(t) = V_0 + V_1 t + V_{max} \left(\frac{t_R}{t}\right)^{1/2} \exp\left[-12D \frac{(t - t_R)^2}{r^2 t}\right] \quad (2.5)$$

where  $V(t)$  = detector voltages which are measured with a digital voltmeter

$V_0 + V_1 t$  = the base line voltage

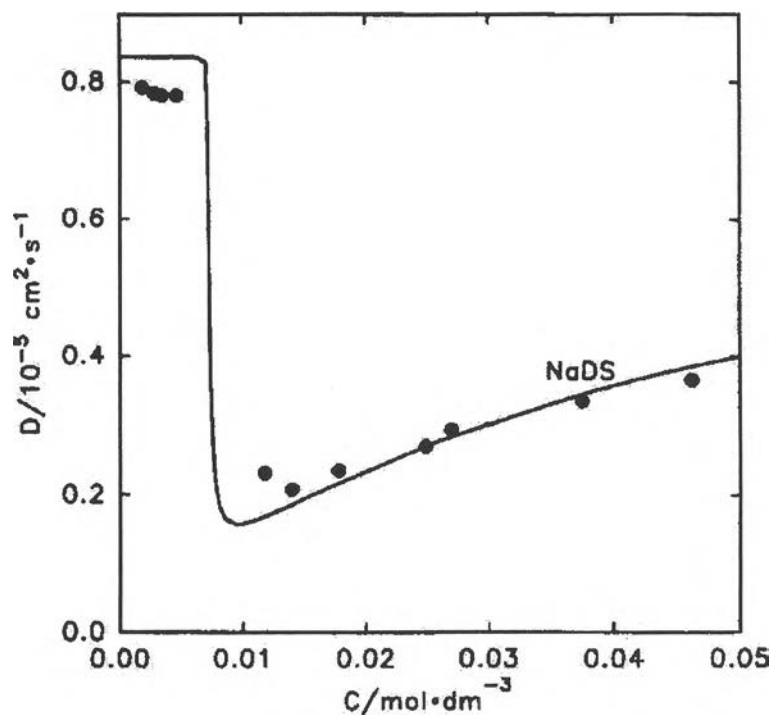
$V_{\max}$  = the peak height

The interesting feature of the Taylor dispersion method is that the diffusion coefficient appears in the numerator of the exponent. As a result, the measured pulse is broad for slow diffusion, and narrow for fast diffusion. This is the antithesis of intuition of the method. It occurs that the radial diffusion is fast compared to convection. This is assured by a very low fluid velocity and a very long thin tube.

## 2.4 Surfactant Diffusivity

Weinheimer *et al.* (1981) measured the diffusion coefficient in water of a nonionic surfactant, Triton X-100, and an ionic surfactant, SDS, as a function of concentration using the Taylor dispersion method by running the experiment above the critical micelle concentration (CMC) at 25 °C. The results showed that, for Triton X-100, the diffusion coefficient dropped as the concentration increased and, for SDS, the diffusion coefficient increased as the concentration increased because of electrostatic coupling between the species present.

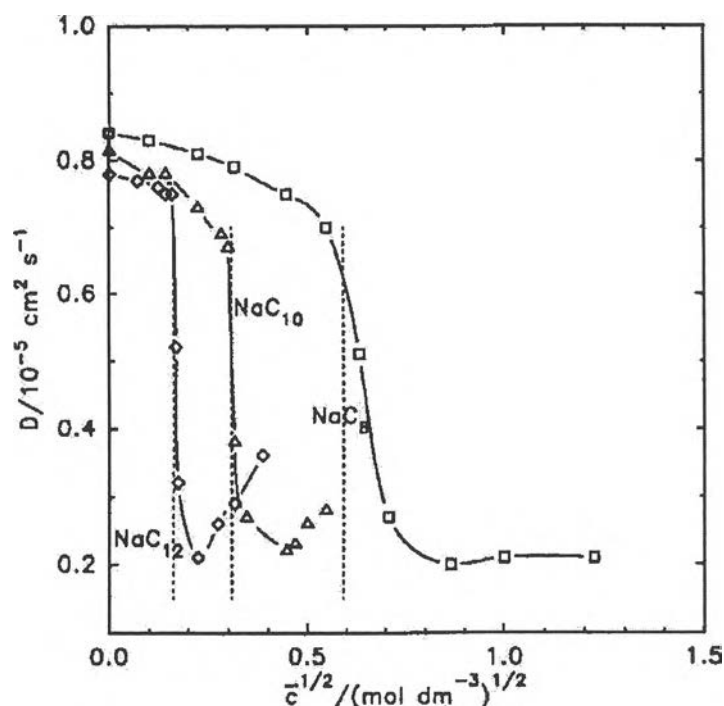
Shortly, after this study, Evans *et al.* (1983) determined diffusion coefficients for tetradecyl trimethyl ammonium bromide (C<sub>14</sub>TAB) at 25, 95 and 130 °C and SDS at 25 °C using the Taylor dispersion method. The results of SDS diffusion coefficients plotted against concentration are given in Figure 2.2.



**Figure 2.2** SDS diffusion coefficients by Taylor dispersion method at 25°C (Evan *et al.*, 1983).

They found that the diffusion coefficient decreased rapidly just beyond the CMC, went through a minimum, and then increased with concentration.

The diffusion coefficients for binary aqueous solution of sodium hexanoate, heptanoate, octanoate, decanoate and dodecanoate salts at 25 °C using the Taylor dispersion method was investigated by Deng *et al.* (1996). Results (Figure 2.3) showed that the diffusion coefficients of sodium hexanoate and heptanoate dropped smoothly as the salt concentration was increased. For each of the longer-chain sodium alkanoates, the diffusion coefficient dropped sharply in the region of CMC.



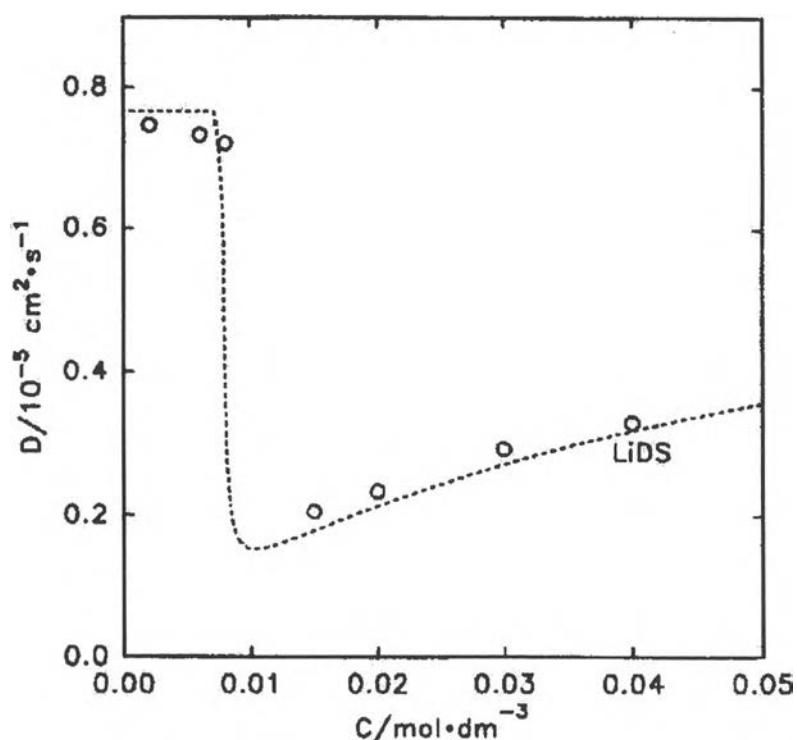
**Figure 2.3** Sodium alkananoates diffusion coefficients by Taylor dispersion method at 25°C (Deng *et al.*, 1996).

It was suggested that the sharp drop in the diffusion coefficients was due to two reasons. Firstly, the formation of micelles reduces the number of free ions diffusing in the solution and this, in turn, reduces the free energy gradient driving the diffusion process. Secondly, the friction acting on a micelle cluster is much larger than that acting on a single surfactant monomer and causes a sharp drop in the diffusion coefficient when micelles occurred at CMC.

Tiberg *et al.* (2000) studied the relation between the capillary flow dynamics and interfacial adsorption. The work was devoted to experimental and theoretical aspects of the capillary rise dynamics exhibited by surfactant solutions in hydrophobic and hydrophilic capillaries. The capillary force was considered to be time-dependent because of surfactant adsorption is a dynamic process, affected by hydrodynamic conditions, mass transport, monomer-micelle conversion rates, and interfacial relaxation. The results showed that, for high CMC surfactants, e.g. C<sub>10</sub>E<sub>6</sub>, the level of liquid in the tube rises much faster than the low CMC surfactants, e.g.

$C_{14}E_6$ . It can be claimed that the surfactant diffusivity of micelle state is slower than the monomer state.

Leaist and Abdu (2001) determined diffusion coefficients for lithium dodecyl sulfate (LiDS) at 25 °C using the Taylor dispersion method. The results are given in Figure 2.4.



**Figure 2.4** LiDS diffusion coefficients by Taylor dispersion method at 25°C (Leaist *et al.*, 2001).

They found that the diffusion coefficient dropped very sharply in the region of CMC and then increased at higher concentration. These results showed the same trend to SDS diffusion coefficient measurements by Evan *et al.* (1983). They explained this unusual diffusion behavior by considering the changes in the mobility and the thermodynamic driving force caused by the association of surfactant ions and counterions to form charged micelles as show in equation (2.6).





This chemical equilibrium model of micelle diffusion gives the binary diffusion coefficient (D) of a univalent ionic surfactant as shown in equation (2.7).

$$D = \frac{c_- c_+ D_- D_+ + q^2 c_- c_m D_- D_+ + n^2 c_+ c_m D_+ D_m}{c_- D_- + c_+ D_+ + (n - q)^2 c_m D_m} \times \frac{c_- + c_+ + (n - q)^2 c_m}{c_- c_+ + q^2 c_- c_m + n^2 c_+ c_m} \quad (2.7)$$

- where
- n = the numbers of surfactant ions per micelles
  - q = the numbers of bound counterions per micelles
  - D<sub>-</sub> = diffusion coefficient of the free surfactant ions
  - D<sub>+</sub> = diffusion coefficient of the free counterions
  - D<sub>m</sub> = diffusion coefficient of the micelles
  - c<sub>-</sub> = concentration of the free surfactant ions
  - c<sub>+</sub> = concentration of the free counterions
  - c<sub>m</sub> = concentration of the micelles