



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Capillary Theory

A capillary tube method can easily be used to determine surface tension of liquids. Cutler and Davis (1975) stated that the height of a liquid in a capillary tube will rise when the tube is immersed in the liquid. Height of the liquid depends on radius of the tube, surface tension of the liquid, density of the liquid, and contact angle between the tube wall, the air, and the liquid. The following equation provides an adequate treatment of the phenomenon.

$$\gamma = \frac{1}{2} grh\rho \quad (2.1)$$

where g is the gravitation constant, h is the height of the liquid rise in the capillary tube, r is the radius of the capillary tube, and ρ is the density of the test liquid. This equation is applicable for contact angle (θ) either 0° or 180° , liquid completely wets the walls of the capillary tube. If contact angle is not 0° or 180° , then Equation (2.1) becomes

$$\gamma \cos(\theta) = \frac{1}{2} grh\rho \quad (2.2)$$

The general attributes of the capillary method have been 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 volume of solution is needed. Although 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 Taylor Dispersion Method

Pratt and Wakeham (1974) introduced the Taylor dispersion (peak-broadening) method in order to measure the mutual diffusion coefficients of sodium dodecyl sulfate (SDS) solutions. In this method, a small sample (20 μ l) was injected into a capillary tube and was carried by a laminar carrier stream of slightly different composition at $25.00 \pm 0.05^\circ\text{C}$. The combination of 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 by

$$\frac{c - \bar{c}}{c_{\max}} = \left(\frac{t_R}{t}\right)^{1/2} \exp\left[-12D \frac{(t-t_R)^2}{r^2 t}\right] \quad (2.3)$$

where D is the effective diffusion coefficient, r is the radius of the tube, c is the average surfactant concentration without the pulse, c is the surfactant concentration averaged across the tube radius at time t , c_{\max} is the maximum value of c , and t_R is the residence time i.e., the tube length divided by the average solution velocity. The diffusion coefficient is obtained by the nonlinear least-square fit of the observed concentration profile.

Leaist and Abdu (2001) proposed an alternative way to monitor the broadened distribution of the injected sample at the outlet of a long capillary tube by using a liquid-chromatography differential refractometer detector. Surfactant diffusivity can be calculated from the least-square fit of the dispersion equation

$$V(t) = V_0 + V_1 t + V_{\max} \left(\frac{t_R}{t}\right)^{1/2} \exp\left[-12D \frac{(t - t_R)^2}{r^2 t}\right] \quad (2.4)$$

to detector voltages, $V(t)$, which are measured with a digital voltmeter at time intervals. Where V_0+V_1t is the base line voltage and V_{\max} is the peak height.

An 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 radial diffusion is fast compared to convection. This is assured by a very low fluid velocity and a very long thin tube.

Leaist and Abbu (2001) studied the diffusion coefficient of SDS and LiDS 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.



This chemical equilibrium model of micelle diffusion gives

$$D = \frac{c_-c_+D_-D_+ + q^2c_-c_mD_-D_+ + n^2c_+c_mD_+D_m}{c_-D_- + c_+D_+ + (n - q)^2c_mD_m} \times \frac{c_- + c_+ + (n - q)^2c_m}{c_-c_+ + q^2c_-c_m + n^2c_+c_m} \quad (2.6)$$

for the self-diffusion coefficient of univalent ionic surfactant. Where n and q are the numbers of surfactant ions and bound counterions per micelle. D_- , D_+ , D_m and c_- , c_+ , c_m are the diffusion coefficients and concentrations of the free counterions, free surfactant ions, and micelles.

Some surfactant diffusivity was determined by the Taylor dispersion method and the Leaist model as shown in Figure 2.1 (Leaist and Abbu, 2001).

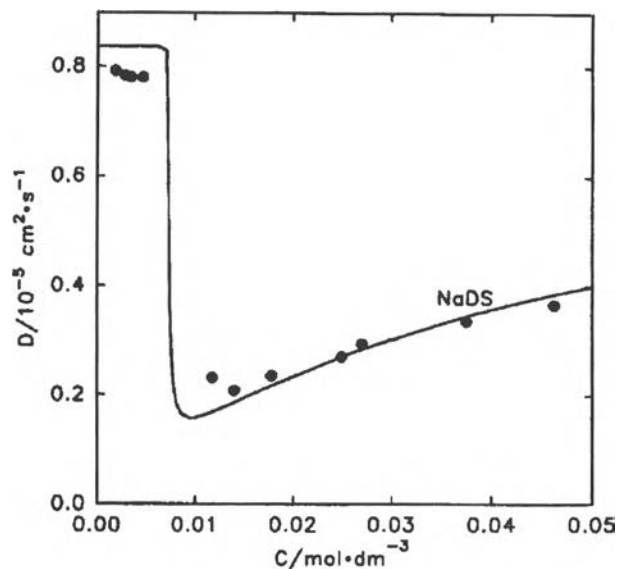


Figure 2.1 Relation between diffusivity of SDS in water and concentration determined by the Taylor dispersion method (●) and Least Model (—) (Leaist and Abbu, 2001).

Figure 2.1 shows the diffusivity of SDS in water at various concentration. Diffusivity of SDS is constant at low concentration and sharply drops at 0.082 mM or critical micelle concentration (CMC) of this surfactant. Diffusivity tends to increase after concentration is above CMC.

2.3 Literature Survey

Weinheimer *et al.* (1981) measured diffusion coefficients 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 CMC at 25 °C. 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.

Three years later, Evans *et al.* (1983) determined diffusion coefficients for tetradecyl trimethyl ammonium bromide (C₁₄TAB) at 25, 95 and 130 °C and SDS at 25 °C using the Taylor dispersion method. They found that the diffusion coefficients

decreased rapidly just beyond the CMC, went through a minimum, and then increased with concentration.

Deng *et al.* (1996) determined diffusion coefficients for binary aqueous solution of sodium hexanoate, heptanoate, octanoate, decanoate and dodecanoate salts at 25 °C using the Taylor dispersion method. Results showed that the diffusion coefficients of sodium hexanoate and heptanoate dropped smoothly as the salt concentration increased. For each of the longer-chain sodium alkanoates, the diffusion coefficient dropped sharply in the region of CMC. 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 occur 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 a 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. C₁₀E₆, the level of liquid in the tube rises much faster than the low CMC surfactants, e.g. C₁₄E₆. It can be claimed that the surfactant diffusivity of the micelle state is slower than the monomer state.

Leaist and Abdu (2001) determined diffusion coefficients for lithium dodecyl sulfate at 25 °C using the Taylor dispersion method. 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 as other works.

Samuhavinyoo (2002) determined diffusivity of SDS by using the transient capillary rise method and pseudo steady-state assumption to develop the model. The result showed that this method is only appropriate to determine diffusivity of SDS at concentration below CMC. Diffusivity of SDS from this work is 2 to 3 times higher

than those reported in literatures because this model is needed to measure the liquid height change inside the capillary tube but this work assumed that the liquid height change inside the capillary tube is a little change so this model is not suitable to measure the liquid height change or it can not obtain SDS diffusivity.