CHAPTER II

LITERATURE REVIEW

Measurements of diffusion data reported in the literature are often difficult to interpret due to inconsistent terminology and lack of clear definitions for the reported diffusion coefficients. Although several different terms are used, there are actually only two general classes of binary diffusion coefficients, the mutual diffusion coefficient and the tracer diffusion coefficient. Even though this study focuses on a special case of mutual diffusion, the mutual diffusion coefficient at infinite dilution, it is important to understand the relationship of our reported diffusion coefficients to other types of diffusion coefficients reported in the literature.

The mutual diffusion coefficient, D_{12}, quantitatively describes diffusion of solute (1) and solvent (2) molecules interacting to equalize concentration gradients and depends only on type 1-2 molecular interactions. The tracer diffusion coefficients D_1^* and D_2^* measure the diffusion of a single species (1 or 2) interacting in a solution of solvent and solute molecules. Therefore, the tracer diffusion coefficient D_1^* depends on both types 1-2 and 1-1 molecular interactions, while D_2^* depends on types 1-2 and 2-2 interactions.

Figure 2.1 illustrates the typical qualitative behavior of both mutual and tracer diffusion as a function of concentration for a generic highly ideal binary system. Several important points can be noted from Figure 2.1;

1. $(D_1^*)^S$ and $(D_2^*)^S$, often referred to as self diffusion coefficients, are limiting cases of the tracer diffusion coefficients, as noted. These quantities are also referred to as D_{11} and D_{22}.

2. Tracer diffusion coefficients are actually strong functions of concentration, although the term 'tracer' is often mistakenly used in reference to only the limiting cases where tracer diffusion approaches mutual diffusion.
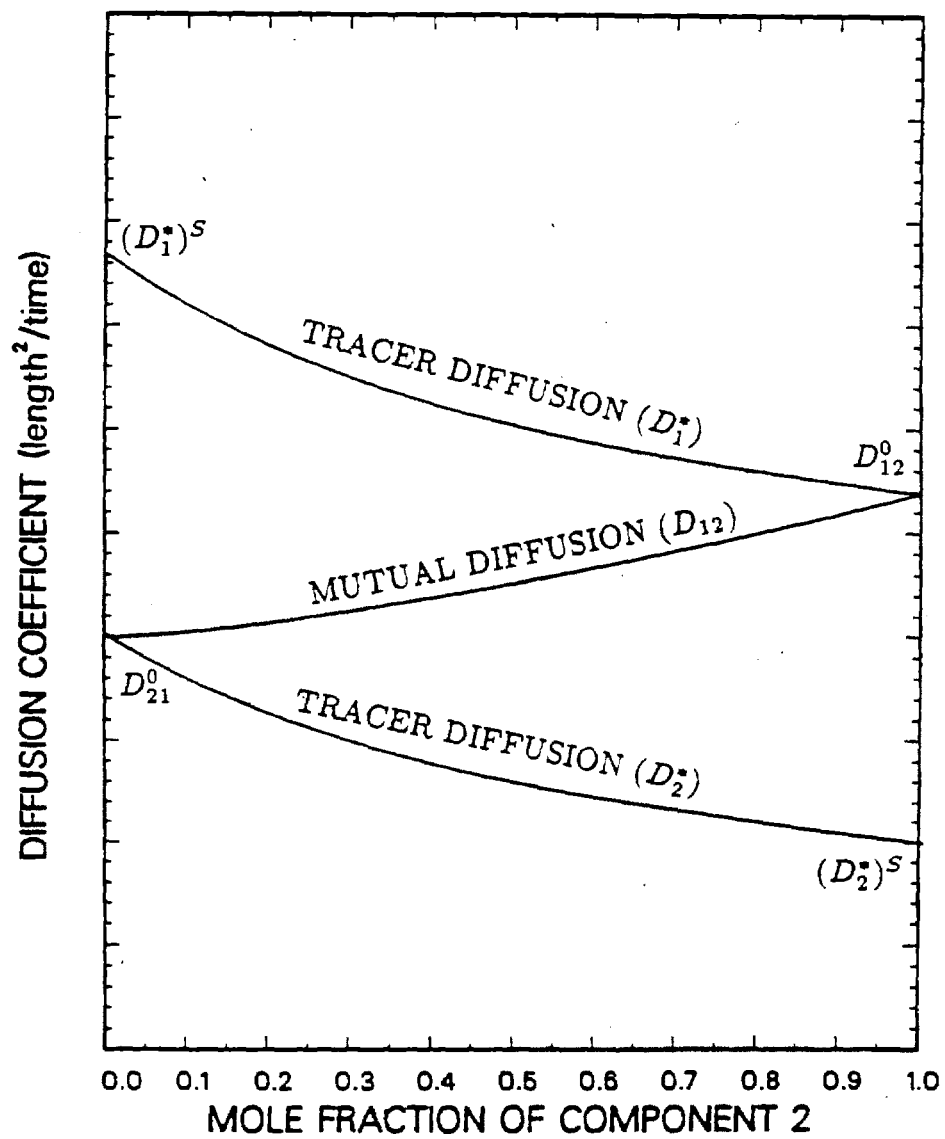
Figure 2.1. Qualitative behavior of diffusion coefficients for a highly ideal binary liquid system.

3. The mutual diffusion coefficient is also a function of concentration. For this study, we have measured several limiting cases of mutual diffusion, properly referred to as 'mutual diffusion coefficients at infinite dilution' or D_{12}^o. Throughout this report we will refer to these limiting cases as simply D_{12}, the diffusion coefficient, or the diffusivity. Except where stated otherwise, these terms have been used interchangeably.

The mutual diffusion coefficient, D_{12}, is the most commonly measured type of diffusion coefficient, and is the diffusion coefficient required for mass transfer calculations. Since most gases are only sparingly soluble in liquids, mutual diffusion coefficients for gases in liquids are always reported as being at infinite dilution. Since liquid-liquid mixtures can exist over the entire concentration range, the effect of concentration on the liquid-liquid mutual diffusion coefficient is often important. However, for the case of diffusion in the Fischer-Tropsch wax, the mutual diffusion coefficient at infinite dilution, D_{12}^o, is the proper diffusion coefficient for mass transfer calculations. In this case, D_{12}^o actually represents the diffusion of infinitely dilute solute, 1, through the FT wax mixture, 2. This is precisely the situation that occurs as a product or reactant diffuses to or from the surface of the FT catalyst.

Section 2.1 of this chapter briefly discusses the experimental techniques that have been used to obtain different types of diffusion coefficients, and shows why there are few data at conditions far removed from ambient. In Section 2.2, the available experimental studies are reviewed. This review is primarily restricted to diffusion in the n–alkane solvents which are the subject of this work. Several predictive equations based on the available data are also discussed in Section 2.2. However, most of these equations are of limited usefulness in high temperature applications because they are based on low temperature data.

2.1 Experimental Techniques

A number of experimental studies of diffusion in liquid alkane systems have been performed near ambient conditions, but few studies report data at elevated temperatures and pressures. This is primarily due to the fact that most experimental methods are not amenable to high temperature and/or pressure measurements. The majority of diffusion data have been obtained using either the diaphragm cell or an optical interference technique. With the diaphragm cell, diffusion takes place across a porous disk, usually made of metal or glass (Figure 2.2). The technique requires placing liquid mixtures of different compositions on either side of the diaphragm in such a way that bulk flow through the diaphragm is eliminated. The objective is to set up a system where molecular diffusion is the only transport mechanism occuring in the cell. By measuring the concentration changes in the liquids on either side of the diaphragm, the diffusion coefficient may be calculated. The calculation requires a precise knowledge of the liquid compositions and of the diffusion path length through the diaphragm. The path length must be calibrated using a system of known diffusivity, and is often a function of the nature of the chemical system being studied. In addition to the exacting calibration requirements, the diaphragm technique is inherently slow, because the time required for diffusion to significantly affect the liquid compositions is usually on the order of days for a typical experiment. The diaphragm cell technique has been used successfully at high pressures, but is not amenable to high temperature measurements because at high temperatures it is difficult to fill and sample the cells without grossly disturbing the liquids. The technique is also poorly suited to the accurate measurement of diffusion coefficients for gaseous solutes. Diaphragm cells are usually used to measure mutual diffusion, but may be used to measure tracer diffusion through the use of

labelled radioactive tracers.

Several optical interference techniques have also been used to measure diffusion coefficients in liquids. Optical interference methods are especially suited to quick measurements of mutual diffusion coefficients over the entire concentration range in a single experiment. Initially, a sharp boundary is set up between two miscible liquids of diferent compositions (Figure 2.2). If all convection is eliminated, then pure diffusion will lead to concentration changes in the region around the original sharp boundary. Using a light source aimed at the boundary, interferometric fringe patterns are created due to sharp gradients in refractive index which occur shortly after the boundary is removed. These fringe patterns may be detected with great precision, especially when a laser is used as the light source. However, due to the inherent experimental difficulties associated with all interferometric techniques, these methods have not yet been extended to high temperatures and pressures. The experimental difficulties lie primarily with establishing the sharp initial concentration gradient, maintaining an optically clear window, and eliminating convection currents.

The self diffusion coefficient, a special case of tracer diffusion is often measured due to its theoretical significance. Self diffusion can be measured using a radioactive tracer and any one of several standard techniques, but is most easily and accurately measured using a special nuclear magnetic resonance (NMR) spin echo method. The NMR spin echo technique requires only small quantities of sample and is easily extended to elevated temperatures and pressures. In the past, the technique has been used primarily to measure self diffusion in pure liquids, but new Fourier transform techniques show promise of allowing the simultaneous determination of as many tracer diffusion coefficients as there are resolvable resonances.

DIAPHRAGM CELL

Disadvantages

1. Slow

2. Calibration of cell required

3. Exact Concentrations Needed

4. Difficult to adapt to extreme conditions

Upper Cell

Porous Disk

Stirrer

Lower Cell
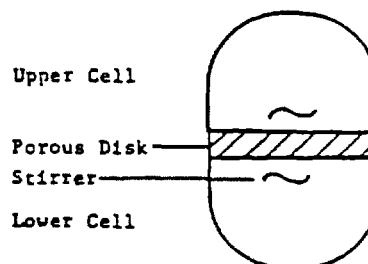
OPTICAL METHODS

Disadvantages

1. Expensive

2. Must have clear container; thus high pressure and temperature difficult.

Optically Clear Container
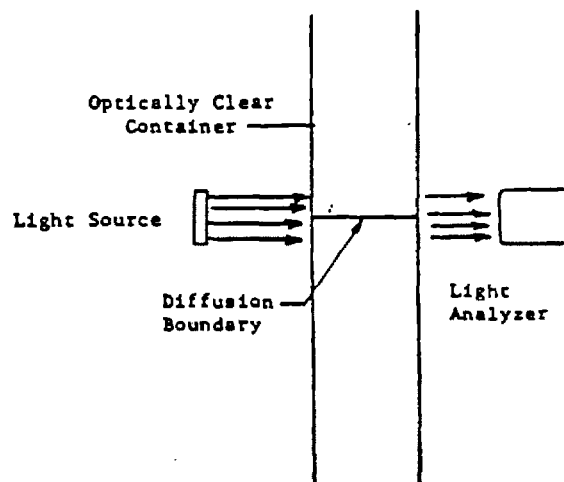
Light Source

Diffusion Boundary

Light Analyzer

Figure 2.2. Illustration of the diaphragm cell and optical interference techniques.

Measuring diffusion of a dissolved gas in a liquid is a special case which presents major experimental difficulties. Malik and Hayduk (1968) devised a special capillary tube technique which has been used by many researchers. Another popular technique for measuring gas-liquid diffusion is the wetted wall column. Even the standard diaphragm cell has been used with some success. The major drawback to all of these methods is that they are highly dependent on accurate gas-liquid solubility data, which is rare, except for the simplest of systems at ambient conditions.

In recent years, the Taylor dispersion method has evolved into the most versatile method for quick and reliable measurements of diffusion coefficients in liquids. The method is a dynamic chromatography technique which has few of the limitations of the other methods. Taylor dispersion is especially amenable to elevated temperature and pressure measurements and can even be used to measure gas diffusivities in liquids without knowledge of gas solubility data. In the past, Taylor dispersion has been used almost exclusively to measure mutual diffusion, but could easily be extended to measure tracer diffusion as well. Since we have chosen the Taylor dispersion technique for this study, a detailed description is given in Chapter IV.

2.2 Experimental Data and Predictive Equations

In this section several experimental studies are reviewed, and some predictive correlations are given. Only the working form of the predictive equations are presented; a detailed discussion of the theoretical bases for these (if any) is given in Chapter III.

Moore and Wellek (1974) studied diffusion coefficients for n-heptane and n-decane in the series of alkane solvents n-hexane through n-decane, and in n-

hexanol and n–heptanol. They studied only the infinitely dilute solute region, at temperatures between 293 and 313 K. A variation on the diaphragm cell method was used, namely the unsteady state porous disk method. Here, a porous disk is filled with a solution of known concentration, then immersed in a well–stirred volume of solvent. Periodic sampling of the solvent as solute leaves the disk is used to follow the diffusion process. This method also requires calibration of an "effective pore length" in the disk. The experimental reproducibility was reported as 5 to 10%. Moore and Wellek (1974) used the empirical hydrodynamic correlation suggested by Hayduk and Cheng (1971) to express diffusivity in alkane and alcohol systems:

$$D_{12} = K_1 \eta^{K_2} \tag{2.1}$$

Although they provide the constants for the systems which they investigated, there is no theoretical or empirical basis for generalizing K_1 and K_2 for other chemical systems. Hayduk and Cheng (1971) suggest that K_1 should be constant for a given solute in any solvent, yet apparently the only way to determine this is from an experiment.

Bidlack *et al.* (1969) used an optical interference technique to study the diffusion of several normal alkanes in the solvents n–heptane and carbon tetrachloride. All measurements were made at 298 K. Van Geet and Adamson (1964) used a diaphragm cell to study both mutual and tracer diffusion for the n–octane/n–dodecane system over the entire range of concentrations at 298 K. They reported that 2 to 4 days were needed for each measurement. Van Geet and Adamson suggested that diffusion in a mixture of homologous alkane solvents is a function of the mean carbon number of the mixture.

Shieh and Lyons (1969) measured mutual and tracer diffusion coefficients in the n–hexane/n–dodecane and n–decane/n–hexadecane systems at 298 and 308 K. They

used both diaphragm cell and an interference technique (Gouy fringe technique). Shieh and Lyons then used their data, along with that of Bidlack and Anderson (1964), Tan (1966), and Van Geet and Adamson (1964) to develop a correlation for diffusivity in alkanes as a function of density ρ and carbon number n:

$$\frac{D_{12}}{q} = K(\rho - 0.84) \tag{2.2}$$

The constant K was shown graphically to be a linear function of the geometric mean of the two carbon numbers of the binary mixture. The thermodynamic factor q corrects for the departure of the mixture from ideal solution behavior:

$$q = 1 + \frac{d \ln f_1}{d \ln x_1} \tag{2.3}$$

where f_1 and x_1 are the fugacity and mole fraction of component 1 in the mixture. For the case of diffusion coefficients at infinite dilution, q is unity. There are two drawbacks to equation (2.2). As will be shown in Chapter V, this equation fails badly at temperatures above 333 K. In addition, to be used to predict diffusivities in mixtures, the thermodynamic terms in equation (2.3) must be known, but accurate predictions are rarely available.

Lo (1974) studied the binary systems n–heptane/n–decane, n–heptane/n–dodecane, n–heptane/n-tetradecane, and n–octane/n–tetradecane. Mutual diffusion coefficients were measured at 297 K over the entire range of concentrations using a diaphragm cell. Lo gave the following relationship between infinite dilution diffusion coefficients and self–diffusivity D_{22} of the solvent:

$$D_{12} = D_{22} + \frac{1}{0.1964 - 0.06785 n_2} \times 10^{-5} \log \frac{n_1}{n_2} \tag{2.4}$$

In this equation, n_1 and n_2 refer to the carbon numbers of the alkane solute and solvent. Aside from the fact that Equation 2.4 is based exclusively on data at 298

K, its use as a predictive tool for D_{12} is limited because the self–diffusivity D_{22} must be known as a function of temperature. There is even less data available for self–diffusion than for mutual diffusion. Van Geet and Adamson (1964) also give several ways of relating D_{12} to the self–diffusivity of the components in the mixture, but the same constraints apply to their equations.

Alizadeh and Wakeham (1982) demonstrated the Taylor dispersion technique in measuring diffusion coefficients for all binary combinations of n–heptane, n–hexane, and n–octane. The data were taken at one atmosphere and temperatures of 290 to 340 K. In contrast to the diaphragm cell, these measurements took on the order of 1 to 3 hours each. This was the first work to extend diffusivity measurements to higher temperatures in alkanes with the Taylor dispersion technique. Alizadeh and Wakeham (1982) fitted their mutual diffusivities in alkanes to the empirical form

$$D_{12} = a_0 + a_1 T - b x_1 \tag{2.5}$$

where T is in Kelvins and x_1 is the mole fraction of the heavier component of the binary mixture. The three coefficients needed to use this equation are particular to each solute/solvent system studied. The authors did not present a general correlation for diffusion in alkane systems.

Recently, Chen and coworkers have demonstrated the utility of the Taylor dispersion technique at even higher temperatures and pressures (Chen and Chen, 1985 a,b, and c; Chen *et al.* 1981; Chen *et al.* 1982; Sun and Chen, 1985 a and b). They have measured mutual diffusion coefficients at infinite dilution for several dissolved gases and spherical solutes at temperatures up to 523 K. Reproducibility of their results was reported to be on the order of 1.0%, but an approximate graphical method was used to determine the value of each individual measurement (see Chapter IV). Their data can be used to extend some existing theories on diffusion

to high temperatures. Chen and Chen (1985b) give an empirical correlation for diffusivities in a variety of systems. For alkane–alkane systems they suggest the following correlation for predictions in the range 273 to 333 K:

$$\frac{10^9 D_{12}\eta_2}{TV_{b2}^{2/3}} = \left(\frac{11.96}{V_{b1}^{1/3}} - 0.8796\right) \tag{2.6}$$

Here, V_b is the molar volume at the normal boiling point for the solute (1) and solvent (2). It is noted that use of this would require the viscosity to be known at high temperatures.

Ertl and Dullien (1973) reported self–diffusivities at temperatures to 433 K for several pure liquids including seven n–alkanes from heptane to octadecane. They suggested several different ways of correlating their self–diffusion data. It was reported that an activated state approach worked well:

$$D_{11} = D_0 \exp(-E/R_g T) \tag{2.7}$$

They give values for D_0 and E (the activation energy) for each alkane and proposed a linear relation between E and carbon number. However, the question of how to extend their observations to mutual diffusion was not addressed. Ertl and Dullien were careful to state that, although an apparent activation energy could be calculated, the model of diffusion as an activated process was not necessarily true. They also found an empirical free volume correlation for the self–diffusion coefficient:

$$D_{11} = C\left(\frac{V - V_o}{V_o}\right)^m \tag{2.8}$$

The values of C, m and V_o were given for several liquids, but again the results were not generalized to mutual diffusion.

Teja (1985) presents correlations for the self and mutual diffusion coefficients based on a corresponding states approach. The correlations were tested only for self–diffusion of n-alkanes. Again, his approach is limited because mutual diffusivities require values for the self–diffusivities.

All of the above studies dealt with diffusion of a solute which is a liquid at normal temperatures and pressures. There are very few relations for predicting diffusivities of dissolved gases in liquid solvents. A review of this subject was given by Himmelblau (1964), and a more recent one by Sovova (1976). Sovova reviewed several hundred data points which were all below 373 K. He recommended the following correlation for diffusion of gases in alkane solvents:

$$D_{12} = \frac{14.8 \times 10^{-5}}{V_g^{0.6}} \times 2.28 \times \eta_2^{-0.5} \qquad (2.9)$$

Here, V_g is the molar volume of the gas at its normal boiling point, and η_2 is the viscosity of the solvent.

Akgerman and Gainer (1972 a,b) proposed an equation for diffusion of gases in liquids which was shown to be superior to other available equations for systems involving small molecules such as H_2. The equation is a modified form of the activated state approach (Glasstone et al., 1941) and has no adjustable parameters.

$$D_{12} = \frac{kT}{\xi_A \eta_2} \left(\frac{N}{V_2}\right)^{1/3} \left(\frac{M_2}{M_1}\right)^{1/2} \exp\left(\frac{E_{\eta 2} - E_{D_{12}}}{R_g T}\right) \qquad (2.10)$$

The various constants in this equation can all be evaluated from geometric considerations and knowledge of viscosity as a function of temperature. Again, the equation is based on ambient temperature data and fails when extended to other temperatures.

Two other predictive equations need mention because of their popularity. These are the Wilke–Chang equation and the Lusis–Ratcliff correlation. While

not specifically developed for alkane systems, they are well known and are routinely used to estimate diffusion coefficients in a wide variety of systems. Both equations are based on an empirical modification of hydrodynamic theory (Chapter III). The Wilke–Chang correlation is (Wilke and Chang, 1955)

$$D_{12}\eta/T = 7.4 \times 10^{-8} \times \frac{(\phi M_2)^{1/2}}{V_1^{0.6}} \qquad (2.11)$$

The arbitrary constant ϕ is the "association constant" which accounts for solvation effects in systems with strong chemical attractions like hydrogen bonds. For alkanes, the association parameter ϕ is usually assumed to be unity. The Lusis–Ratcliff (1968) equation is similar to the Wilke–Chang equation:

$$D_{12}\eta/T = 8.52 \times 10^{-10}(V_2)^{-1/3}\left[1.40(\frac{V_2}{V_1})^{1/3} + (\frac{V_2}{V_1})\right] \qquad (2.12)$$

It is apparent from the above review that there are few high temperature data available (T > 373 K). Consequently, most of the correlations and predictive equations have not been tested at high temperatures. The only recourse for the design engineer is to extrapolate the existing data base or use the equations far out of their proven range of applicability.