CHAPTER I

INTRODUCTION

Basic chemical engineering processes such as gas absorption, membrane separation, heterogeneous reactions, etc. cannot be adequately modelled without accurate estimates of diffusion coefficients in the liquid phase. Still, very few measurements of diffusion coefficients in liquids at temperature and pressures above ambient have been published and theories to predict diffusion coefficients in liquids are not well established. Consequently, existing correlations often yield poor predictions of diffusion coefficients at the elevated temperatures and pressures where the majority of chemical processes operate. The U.S. Department of Energy has expressed a specific concern that estimates of diffusion coefficients used to model the Fischer-Tropsch process may be highly erroneous. The primary purpose of this research was to measure diffusion coefficients for several solutes in an actual sample of Fischer-Tropsch reactor wax at typical reaction conditions.

The Fischer-Tropsch Synthesis is a process by which gasoline, diesel oil, wax, and alcohols are produced from hydrogen and carbon monoxide. Coal is usually gasified to supply the required hydrogen and carbon monoxide. These two gases are then reacted in either a gas/solid fixed bed or fluidized bed reactor, or in a liquid slurry containing a suspended catalyst. In addition to the primary products, carbon dioxide is formed as a side product by the water-gas shift reaction. Literature on the process is voluminous. The interested reader is referred to Anderson (1984), Riekena et al. (1982), and Baird et al. (1980), as a starting point.

The Fischer-Tropsch synthesis reaction has been studied in many different types of reactors, at several different conditions, and with various catalysts. In order to evaluate mass transfer characteristics in these various systems, accurate estimates of liquid phase diffusion coefficients for products and reactants are critical.

The task of estimating diffusion coefficients in a Fischer-Tropsch reactor is by no means elementary. The steady state liquid phase, often referred to as FT wax, is primarily a mixture of saturated hydrocarbons with an average carbon number of about 30, although it can range as high as 70. The melting point of the FT wax is typically in excess of 100°C, and reaction conditions of the normal process range from 473-573 K at 1 to 5 MPa. Prior to this study, diffusion coefficients in even the simplest pure low melting hydrocarbons had not been measured at these conditions. For this reason, we began our research by measuring diffusion coefficients in pure low molecular weight hydrocarbon solvents and progressed to measure diffusion in higher molecular weight solvents until we were ultimately able to measure diffusion coefficients in an actual sample of FT reactor wax.

The experimental work was performed in three phases. During the first phase of the project, we constructed a Taylor dispersion apparatus. This apparatus was then used to measure infinite dilution diffusion coefficients of the normal alkane solutes octane, decane, dodecane, tetradecane, and hexadecane, and of the gases hydrogen, carbon monoxide, and carbon dioxide in the n–alkane solvents heptane (C_7), dodecane (C_{12}), and hexadecane (C_{16}). Normal alkanes were chosen because they are a simple homologous series and are primary products of the FT synthesis. Hydrogen and carbon monoxide are reactants in the synthesis and carbon dioxide is a product of the water–gas shift. Measurements were made at temperatures between 298 and 573 K, and pressures from 0.1 to 3.45 MPa (14.7 to 500 psia). Prior to this study, the available data for alkane/alkane systems were primarily limited to the temperature range 290–343 K, and there were no data available for the diffusion of gases above 323 K.

The solvents chosen for the first phase of the project were all liquids at ambient conditions. During the second phase of the project, we modified the Taylor dispersion apparatus so that we could collect data at similar conditions using solvents which are solids at room temperature. We proceeded to measure diffusion coefficients in the solvents n–eicosane (C_{20}) and n–octacosane (C_{28}) at several temperatures ranging from 373 to 534 K. Prior to this study, diffusion coefficients had never been measured in these solvents which have melting points of 36 and 60°C respectively.

During the third and final phase of the experimental work, we measured mutual diffusion coefficients at infinite dilution for each of the selected alkane and gaseous solutes in an actual sample of FT wax which melted near 100°C. Measurements were made at 200 psia over the range 473–533 K, which are typical FT reactor conditions.

Throughout the experimental portion of the project, we also made several important contributions in the area of experimental techniques for measuring the thermophysical properties of fluids. We constructed the first Taylor dispersion apparatus capable of measuring diffusion coefficients at high temperatures and pressures in liquids which are solids at ambient conditions. This apparatus was designed for automatic operation and data acquisition so that a large number of experiments could be performed in as short a time as possible. In addition to diffusivity data, it was necessary to determine the viscosity of the solvent at the temperature and pressure of the experiment so that certain predictive theories which require solvent viscosity could be tested. Since viscosity data were not available over the entire range of conditions, we constructed a high temperature, high pressure viscometer to work in conjunction with the diffusion apparatus. Certain theoretical treatments have shown that the diffusion coefficient is also related to the molar volume of the solvent. Therefore, another goal of this work was to obtain reliab measurements of solvent density, from which molar volume is calculated. We developed and demonstrated a novel technique for density measurement which is based on the theory of the Taylor dispersion apparatus. During the course of the project, we also developed a computer model for analyzing Taylor dispersion data which is superior to previous models and an improved technique for collecting gaseous solute data using the Taylor dispersion apparatus.

Following the completion of the experimental work, we developed a correlation for predicting the diffusion coefficients of alkanes and gases in alkane solvents ranging from C_7 to C_{28}. The applicability of this equation to Fischer–Tropsch wax solvents was tested by using bulk properties of the wax to predict diffusion coefficients in the wax.