# Infinite Dilution Mutual Diffusion Coefficients of 1-Octene and 1-Tetradecene in Near-Critical Ethane and Propane

**James M. Noel, Can Erkey, Dragomir B. Bukur, and Aydin Akgerman***

Chemical Engineering Department, Texas A&M University, College Station, Texas 77843-3122

We have utilized the Taylor dispersion technique to measure the infinite dilution mutual diffusion coefficients of 1-octene and 1-tetradecene in subcritical and supercritical ethane and in subcritical propane in the temperature range 293.15–338.15 K and the pressure range 5.52–11.03 MPa. For ethane, the measurements were done on either side of the critical temperature with the pressure above the critical pressure.

## Introduction

The Fischer–Tropsch synthesis (FTS) is a method for converting synthesis gas into petroleum products such as gasoline and diesel fuel. The FTS can be carried out in the gas phase using fixed bed reactors or in the liquid phase in a slurry reactor. Effective pore diffusion is a rate-controlling phenomenon in both reactor types. In the fixed bed reactor, product accumulation in the pores of the catalyst results in liquid-filled pores which hinder diffusion of the gas-phase reactants. This problem may be eliminated by using a supercritical fluid as a solvent where high molecular weight hydrocarbons can be extracted in situ (Yokota and Fujimoto, 1989, 1991). In order to model catalytic performance of the supercritical phase FTS, the effective diffusivities of reactants and products in the catalyst pores should be known. Effective diffusivities can be fairly accurately estimated if the molecular diffusion coefficients are known. However, data on diffusivities in supercritical fluids are scarce, and most predictive techniques do not work in the near-critical region. In this work we present data on the limiting mutual diffusion coefficients of representative Fischer–Tropsch products, 1-octene and 1-tetradecene, in propane and ethane in the near-critical region.

## Experimental Method

We used the Taylor dispersion technique to determine the infinite dilution mutual diffusion coefficients (Taylor, 1953). In this technique, a pulse of solute dissolved in the solvent is injected into a tube in which the solvent is moving in laminar flow. The pulse is dispersed due to combined action of convection in the axial direction and diffusion in the radial direction. Eventually, the peak elutes from the end of the tube where a suitable detector is employed to measure the radially averaged concentration profile as a function of time. Diffusion coefficients are extracted by analysis of the profiles. Detailed reviews of the criteria for design and operation of a Taylor dispersion apparatus are given by Alizadeh et al. (1980) and Erkey and Akgerman (1991). A schematic diagram of our experimental setup is given in Figure 1. The syringe pump (Isco, LC-260) is filled with liquid solvent from the supply bottle. A carbon bed placed in the supply line is used to remove any impurities in the solvent. The dispersion tube is 15.24 m long with an internal diameter of 0.524 mm. The tube is coiled for effective temperature control, and the diameter of the coil is 0.457 m. Flow is started through the dispersion tube, and after a steady flow is achieved, a pulse of solute–solvent mixture (~10 mol %), pressurized to the experimental conditions, is injected through the injection valve (Rheodyne Model 7010). The sample loop size is 20 μL. A UV detector (ISCO V-4) at the end of the dispersion coil is used to detect the eluting solute peak. Pressure is controlled with two back-pressure regulators (Tescom Inc. 26-1722-24-084 and Grove SD91-W) placed in series after the UV detector. Two regulators are necessary to minimize pulsation. The stream from the regulator is passed through a dry gas meter (Singer DTM-115), and finally it is vented to the atmosphere. Further details of the experimental setup with experimental verification of the design criteria are given elsewhere (Noel, 1994).

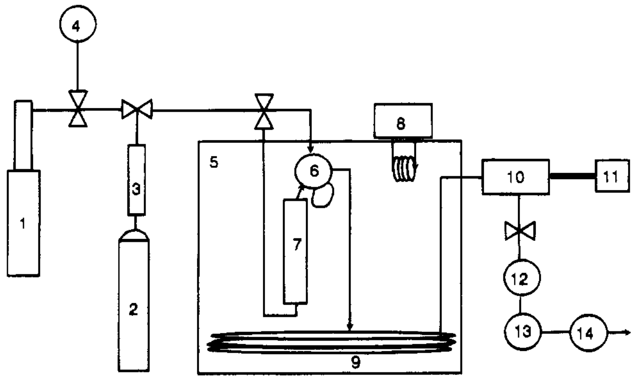

**Figure 1.** Schematic diagram of the Taylor dispersion apparatus: 1, syringe pump; 2, gas cylinder; 3, carbon bed; 4, pressure transducer; 5, water bath; 6, injection valve; 7, sample volume; 8, immersion circulator; 9, diffusion coil; 10, UV detector; 11, data acquisition; 12, back-pressure regulator; 13, back-pressure regulator; 14, dry gas meter.

Solutes were chosen that would represent a wide variety of FTS products. Because the goal of the FTS is production of long-chain hydrocarbons, we focused on compounds with carbon numbers from 8 to 14. The availability of a UV detector prompted using readily available olefins, namely, 1-octene and 1-tetradecene (Aldrich Chemical Co.). Ethane and propane were chosen as solvents. Since ethane has a critical temperature of 305.40 K and a critical pressure of 48.8 bar, experiments could be performed easily above and below the critical temperature while remaining above the critical pressure. This allowed the study of diffusion in the critical and subcritical regions. Ethane had a purity of 95+%. Propane was also chosen because it is the solvent we are actually testing in the FTS. Experiments in

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* To whom correspondence should be addressed.

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**Table 1. Infinite Dilution Mutual Diffusion Coefficients**

| $T$/K | $P$/bar | $\varrho$/(kg·m$^{-3}$) | $10^9 D_{12}$/(m$^2$·s$^{-1}$)[a,b] |
|---|---|---|---|
| | | 1-Octene in Ethane | |
| 296.2 | 112 | 399.1 | 12.6 ± 0.3 |
| 296.2 | 90.4 | 388.6 | 13.5 ± 0.0 |
| 296.2 | 70.7 | 376.2 | 14.2 ± 0.2 |
| 311.2 | 91.0 | 350.1 | 15.6 ± 0.8 |
| 317.1 | 91.1 | 330.2 | 17.0 ± 0.4 |
| 322.2 | 90.3 | 308.4 | 18.1 ± 0.4 |
| | | 1-Tetradecene in Ethane | |
| 293.2 | 112 | 404 | 9.99 ± 0.09 |
| 294.2 | 90.4 | 393 | 10.7 ± 0.2 |
| 297.9 | 91.2 | 385 | 10.7 ± 0.6 |
| 293.4 | 69.0 | 383 | 11.1 ± 0.1 |
| 308.2 | 91.4 | 359 | 12.5 ± 0.7 |
| 310.9 | 90.0 | 350 | 13.3 ± 0.1 |
| 315.2 | 89.8 | 335 | 14.6 ± 0.1 |
| 319.2 | 90.6 | 321 | 15.4 ± 0.1 |
| 322.2 | 90.2 | 308 | 17.4 ± 0.3 |
| | | 1-Octene in Propane | |
| 296.5 | 91.7 | 514 | 7.71 ± 0.10 |
| 308.2 | 91.0 | 501 | 8.88 ± 0.28 |
| 322.5 | 93.4 | 482 | 9.60 ± 0.14 |
| 337.5 | 93.4 | 461 | 11.1 ± 0.3 |
| 296.5 | 55.6 | 506 | 7.77 ± 0.45 |
| 308.2 | 57.1 | 491 | 8.56 ± 0.17 |
| 322.5 | 56.2 | 472 | 10.2 ± 0.1 |
| 337.5 | 55.6 | 444 | 12.0 ± 0.6 |
| | | 1-Tetradecene in Propane | |
| 292.5 | 91.4 | 518 | 5.74 ± 0.04 |
| 293.2 | 91.1 | 517 | 6.18 ± 0.07 |
| 303.2 | 90.1 | 506 | 6.32 ± 0.05 |
| 308.2 | 89.6 | 500 | 6.83 ± 0.20 |
| 313.2 | 88.9 | 494 | 6.99 ± 0.04 |
| 322.5 | 90.7 | 483 | 7.88 ± 0.11 |
| 329.4 | 92.0 | 474 | 8.07 ± 0.11 |
| 337.2 | 89.6 | 462 | 8.79 ± 0.17 |

[a] The ± value is 1 standard deviation. [b] Calculated from Starling (1973).

propane were in the subcritical region in temperature due to equipment limitations, although the pressure was kept above the critical pressure. Propane had a purity of 99.5%.

## Results

The infinite dilution mutual diffusion coefficients of 1-octene and 1-tetradecene in near-critical ethane and propane are given in Table 1. Temperatures range from 293.15 to 338.15 K, and the pressures are in the range 5.5–11.2 MPa. During diffusion measurements, the pressure was held constant at approximately 9 MPa and the temperature was varied to determine the density dependence of the diffusion coefficients, except for diffusion in ethane at temperatures below 298 K, where the density was varied by changing the pressure. Each entry in Table 1 represents at least three repetitive measurements. The reported uncertainties are 1 standard deviation. Experiments for 1-octene in propane were made at two pressures, 5.6 and 9.2 MPa. It was found that the diffusion coefficients were a strong function of density in the temperature and pressure ranges investigated. Figures 2 and 3 present the diffusion coefficients as a function of density; the data at different temperatures and pressures do correlate with density. In addition, it seems like the liquid-phase data can be extrapolated to the supercritical region for diffusion in ethane, although more data are needed to verify this observation.

## Conclusions

The infinite dilution mutual diffusion coefficients of 1-octene and 1-tetradecene have been measured in ethane and propane using the Taylor dispersion technique. This work has provided some of the first data for these compounds at the experimental conditions. The data were obtained on either side of the critical temperature while at supercritical pressures for ethane, and the data indicate linear variation with respect to density.

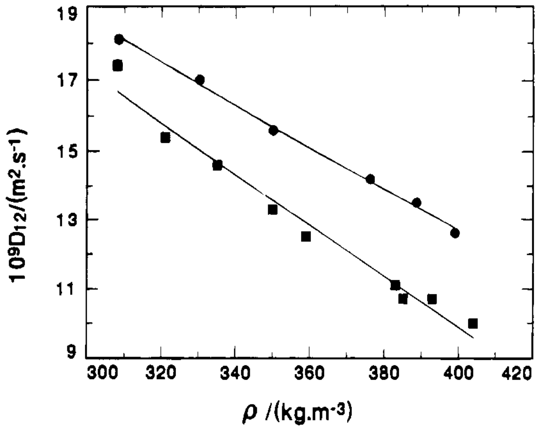

**Figure 2.** Density dependence of the infinite dilution mutual diffusion coefficients of 1-octene and 1-tetradecene in subcritical and supercritical ethane: ●, octene; ■, tetradecene.

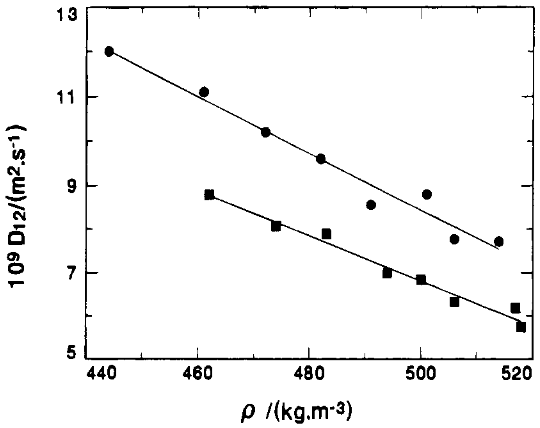

**Figure 3.** Density dependence of the infinite dilution mutual diffusion coefficients of 1-octene and 1-tetradecene in near-critical propane: ●, octene; ■, tetradecene.

## Literature Cited

Alizadeh, A. A.; Nieto de Castro, C. A.; Wakeham, W. A. The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements. *Int. J. Thermophys.* **1980**, *1*, 243.

Erkey, C.; Akgerman, A. Taylor Dispersion. In *IUPAC Volume on Measurement of the Transport Properties of Fluids: Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers, J. V., Eds.; Blackwell Scientific Publications: Oxford, Great Britain, 1991; Vol. III, Chapter 9.

Noel, J. M. The Limiting Mutual Diffusion Coefficients of Fischer-Tropsch Synthesis Products in Near-Critical Hydrocarbons. M.S. Thesis, Texas A&M University, 1994.

Starling, K. E. *Fluid Thermodynamic Properties for Light Petroleum Systems*; Gulf Publishing Co.: Houston, TX, 1973.

Taylor, G. I. Dispersion of Soluble Matter in Solvent Flowing Slowly through a Tube. *Proc. R. Soc. London* **1953**, *A219*, 186.

Yokota, K.; Fujimoto, K. Supercritical Phase Fischer-Tropsch Synthesis Reaction. 2. The Effective Diffusion of Reactant and Products in the Supercritical Phase Reaction. *Ind. Eng. Chem. Res.* **1991**, *30*, 95–100.

Yokota, K.; Fujimoto, K. Supercritical Phase Fischer-Tropsch Synthesis Reaction. *Fuel* **1989**, *68* (2), 255–256.

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