FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I.   Objectives for the First Quarter, Year 4:

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

Our objectives for this quarter were to attempt to develop a model to predict the molecular diffusion coefficients to a high degree of accuracy so we may be able to predict both the molecular diffusion coefficient and thus the effective diffusivity *a priori*. We are working on a semi-empirical equation based on the rough hard sphere theory to predict diffusion coefficients in supercritical fluids. In addition we planned to take additional data in order to extent the database available for development of the predictive equation.

II.   Accomplishments and Problems, First Quarter, Year 4:

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

In predicting diffusion in fluids (gases or liquids) the kinetic theory and its extension to dense gases is widely used. In its application to diffusion prediction in liquids the rough hard spheres model is used. According to this approach the infinite dilution diffusion coefficient, D_{12}, is assumed to equal to the rough hard sphere diffusivity. The equation is given as:

$$D_{12} \approx D_{12,RHS} = A_{12} D_{12,SHS} \qquad (0 < A_{12} \leq 1) \qquad (1)$$

In this equation $D_{12,SHS}$ is the smooth hard sphere diffusivity which is multiplied by a factor A_{12}, called roughness factor, to correct it for interchange of translational and rotational momentum. The equation is frequently expressed as:

$$D_{12,RHS} = A_{12}\left(\frac{D_{12,SHS}}{D_{12,E}}\right)_{MD} D_{12,E} \qquad (0 < A_{12} \leq 1) \qquad (2)$$

Here $D_{12,E}$ is the Enskog Diffusivity for gases and the ratio $(D_{12,SHS}/D_{12,E})_{MD}$ is the so called correction factor to the Enskog Diffusivity that can be obtained from molecular dynamics simulations. The Enskog dense gas theory is well developed and the equation is:

$$D_{12,E} = \frac{D_{12,HSG}}{g(\sigma_{12})} \qquad (3)$$

The term $D_{12,HSG}$ is the diffusion coefficient for a dilute collection of hard spheres or a hard sphere gas. This was developed by Chapman and Enskog (1970) to the following equation:

$$D_{12,HSG} = \frac{3}{8n_2\sigma_{12}^2}\left[\frac{kT}{2\pi}\frac{(m_1+m_2)}{m_1m_2}\right]^{\frac{1}{2}}$$ (4)

The rough hard spheres diffusivity is then given by:

$$D_{12,RHS} = \frac{3}{8n_2\sigma_{12}^2}\left[\frac{kT}{2\pi}\frac{(m_1+m_2)}{m_1m_2}\right]^{\frac{1}{2}}\frac{1}{g(\sigma_{12})}\left[\frac{D_{12,SHS}}{D_{12,E}}\right]_{MD} A_{12}$$ (5)

The correction factor to the Enskog dense gas equation, $(D_{12,SHS}/D_{12,E})$, which is calculated by molcular dynamics, is a function of molecular sizes, masses, and molar volume of the system.

$$\left(\frac{D_{12,SHS}}{D_{12,E}}\right)_{MD} = F\left(\frac{m_1}{m_2},\frac{\sigma_1}{\sigma_2},\frac{V}{V_o}\right)$$ (6)

It is shown that the correction factor for mutual diffusion at infinite dilution is approximately equal to that for self diffusion.

$$\frac{V}{V_o}\left(\frac{D_{12,SHS}}{D_{12,E}}\right)_{MD}\frac{1}{g(\sigma_{12})} \approx \frac{V}{V_o}\left(\frac{D_{22,SHS}}{D_{22,E}}\right)_{MD}\frac{1}{g(\sigma_{22})}$$ (7)

Then fitting available self diffusion data in the literature, the following relationship is observed:

$$\frac{V}{V_o}\left[\frac{D_{22,SHS}}{D_{22,E}}\right]_{MD}\frac{1}{g(\sigma_{22})} = a\left[\frac{V}{V_o}-b\right]$$ (8)

Chen et al. (1982) and Matthews and Akgerman (1987) were then able to reduce the rough hard spheres equation to the following functionality:

$$D_{12} = \beta\sqrt{T}\left(V-V_D\right)$$ (9)

where β is a constant dependent on both the solvent and solute properties. The variable V_D is a property very closely related to the close packed solvent volume denoted by V_o. Erkey et al. (1990) used a similiar approach to fit self diffusion data for supercritical fluids and obtained a similar relationship:

$$\frac{V}{V_o} \left[\frac{D_{22,SHS}}{D_{22,E}} \right]_{MD} \frac{1}{g(\sigma_{22})} = 2.19 \left[\left(\frac{V}{V_o}\right)^{\frac{2}{3}} - 1.271 \right] \tag{10}$$

This allowed for equation (9) to be represented as:

$$D_{12} = \beta \sqrt{T} \left(V^{\frac{2}{3}} - 1.271 V_o^{\frac{2}{3}} \right) \tag{11}$$

where the value of 2.19 is lumped into the β parameter.

However, both equations (9) and (11) do not predict our data and literature data on infinite dilution diffusion in supercritical fluids. However, self diffusion of similar species can be predicted by equation (11). Therefore, a form similiar to equation (11) can be posrulated to predict binary diffusion coefficient data.

$$D_{12} = \beta \sqrt{T} \left(V^{\alpha} - V_o^{\alpha} \right) \tag{12}$$

This equation keeps the general form of equation (11) and still specifies the close packed molar volume as the intercept. However now both α and β depend on the solvent and solute molar properties. In previous papers (Erkey et al., 1990; Akgerman et al.,1996) the values of α and β were shown to have strong correlations to certain functionalities. These were:

$$\beta = f\left(\frac{m_1}{m_2} \right) \tag{13}$$

$$\alpha = f\left(\frac{\sigma_1}{\sigma_2} \right) = \frac{\sigma_2}{\sigma_1} - \frac{1}{3} \tag{14}$$

where the effective hard sphere diameters were calculated by the Purkait and Majumdar (1981) correlation. As seen equation (14) reduces to the expected value of $\alpha = 2/3$ for self diffusion as reported by Erkey et al. (1990). The functionality of α is taken to be an absolute for all solvent/solute interactions. Thus for a given system all that need be determined is the functionality of the parameter β. We have used the data we have taken and reported through the course of this project and additional data summarized below and correlated β with the molecular mass ratio of the solvent and the solute using only our data.

Data were collected for diffusion of 1-octene in solvents supercritical ethane, propane, and hexane. These data are presented in Tables 1-3. Figure 1 shows the trend of the data with respect to the molar volume. The values of β were then fit by a non-linear regression to express the correlation as:

$$\beta = \left(0.05 \left(\frac{m_1}{m_2} \right)^{1.8856} \right) \bullet 10^{-9} \qquad (15)$$

This follows theory since it was expected that β would be a strong function of molecular weight. Equation (15) is specific for this system of fluids and should only be used for similiar systems of diffusion of heavy molecular weight hydrocarbons in low molecular weight hydrocarbons. Figure 2 shows prediction of experimental data for this study. The prediction, as expected, is accurate, however these data were used to determine the β functionality. Figure 3 shows prediction of experimental data from the literature. In figure 3 all predictions fall within the range of experimental error for the prediction of benzene and its derivatives in n-hexane.

III.   Plans for the Second Quarter, Year 4:

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

We will continue our studies on developing a predictive equation for *a priori* prediction of diffusion in supercritical fluids and if necessary obtain more data to verify the theoretical approach.

References:

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Matthews, M. A.; Akgerman, A. "Diffusion Coefficients for Binary Alkane Mixtures at Temperatures to 573 K and Pressures to 3.5 MPa", *AIChE J.*, 1987, 33, 881.

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Table 1. Diffusion Coefficients of 1-Octene in Ethane

T/K	P/bar	$\rho/kg\ m^{-3}$	Molar Volume/ $m^3\ mol^{-1}$	$10^9\ D_{12}/m^2s^{-1}$
322	124.1054	349.9	85.8703	13.26 ± 0.625
340	124.1054	299.9	100.1867	18.52 ± 0.940
357	124.1054	249.2	120.5698	22.67 ± 0.612
378	124.1054	199.9	150.3052	31.12 ± 0.346
414	124.1054	150.5	199.6412	37.61 ± 2.515
503	124.1054	100.9	297.7800	55.49 ± 4.476

Table 2. Diffusion Coefficients of 1-Octene in Propane

T/K	P/bar	$\rho/kg\ m^{-3}$	Molar Volume/ $m^3\ mol^{-1}$	$10^9\ D_{12}/m^2s^{-1}$
314	124.1054	500.7	88.0647	9.112 ± 0.288
354	124.1054	450.7	97.8345	11.81 ± 0.393
384	124.1054	401.1	109.9327	14.31 ± 0.746
408	124.1054	350.2	125.9109	16.29 ± 0.547
429	124.1054	300.6	146.6866	22.70 ± 0.843
453	124.1054	249.6	176.6587	26.88 ± 0.664
485	124.1054	200.6	219.8106	34.59 ± 0.640
544	124.1054	150.4	293.1782	44.88 ± 0.395
523	62.0527	73.64	598.7778	66.89 ± 1.610
533	62.0527	71.31	618.3425	68.77 ± 3.551
543	62.0527	69.18	637.3808	70.61 ± 0.451

Table 3. Diffusion Coefficients of 1-Octene in Hexane

T/K	P/bar	ρ/kg m^{-3}	Molar Volume/ m^3 mol^{-1}	10^9 D$_{12}$/m^{2}s^{-1}
483	124.1054	500.2	172.2711	13.90 ± 0.325
523	103.4212	437.7	196.8700	17.50 ± 0.110
523	82.7369	416.5	206.8908	18.30 ± 0.715
523	62.0527	381.6	225.8124	21.20 ± 1.521
523	44.8158	312.1	276.0974	26.70 ± 2.336
563	62.0527	257.2	335.0311	35.00 ± 2.755
563	44.8158	149.8	575.2336	57.10 ± 3.145

Exp.Res.
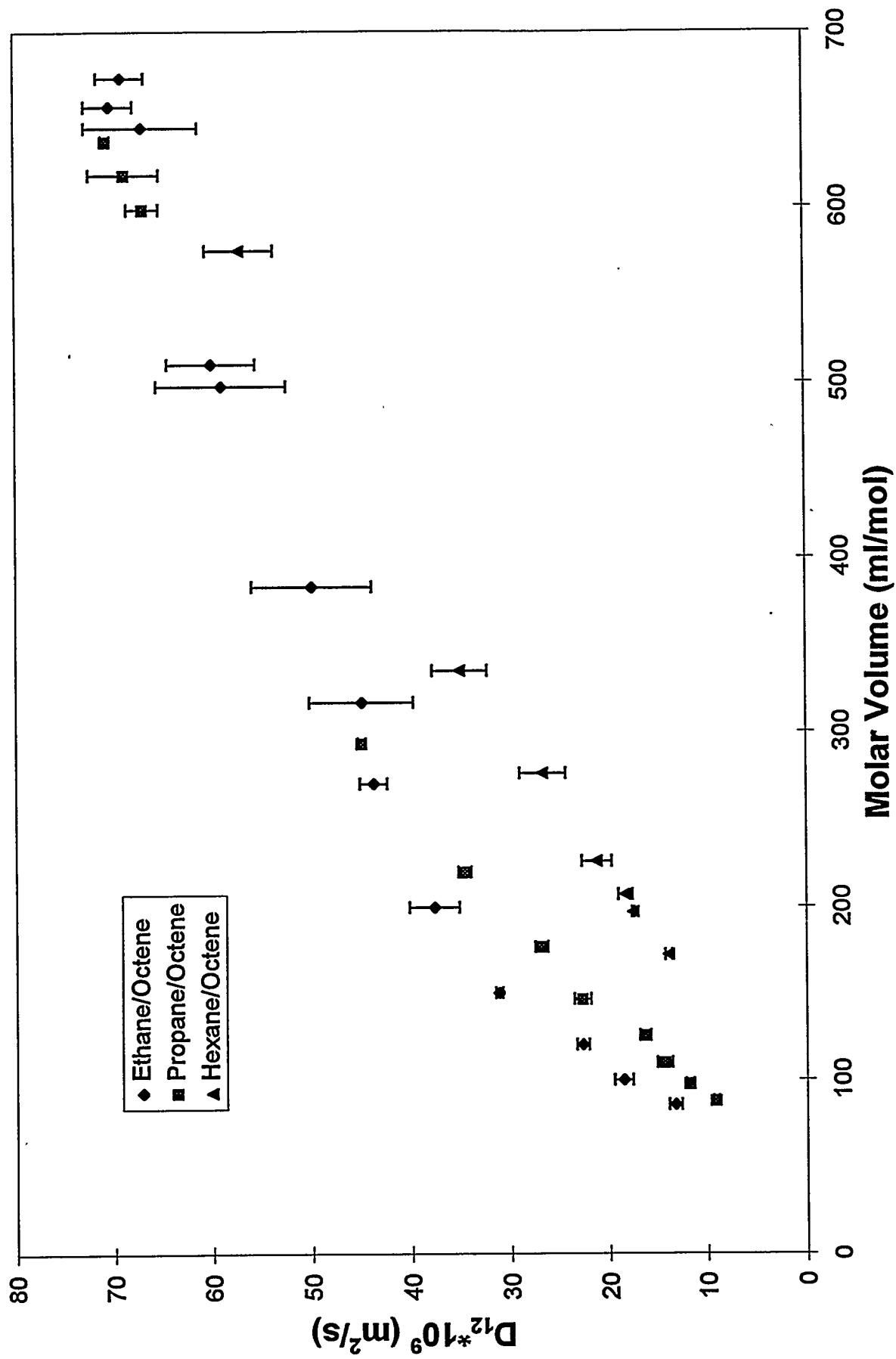
Comparison of Experimental and Predicted Diffusion Coefficients for Data in this Study

Legend:
- ◆ Ethane/Octene
- ▲ Propane/Octene
- ■ Hexane/Octene

x-axis: Molar Volume (ml/mol)

y-axis: $D_{12} * 10^9$ (m²/s)
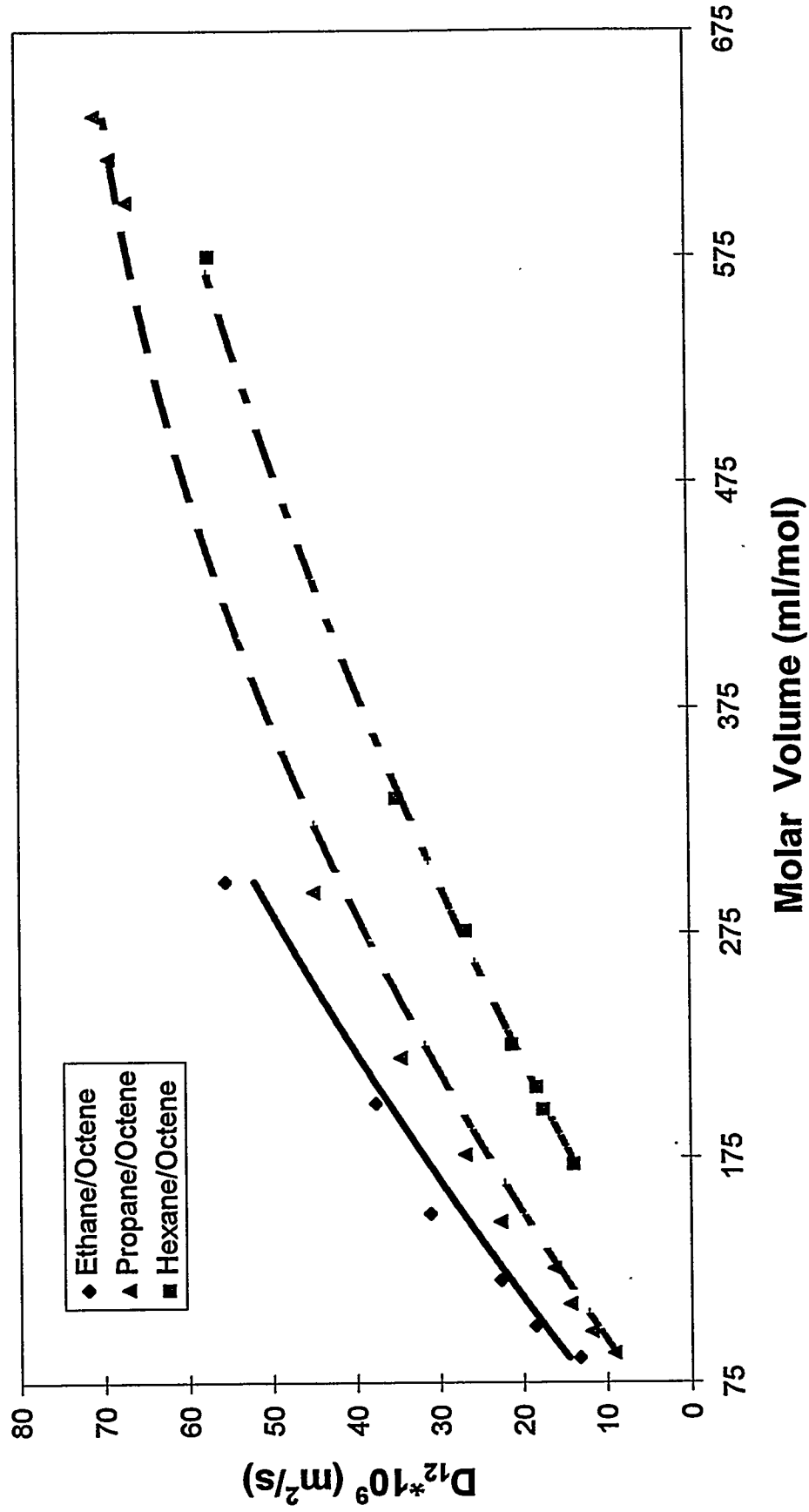
Diffusion Coefficients
for n-Hexane Data in the Literature

Legend:
- ◆ Hexane/Benzene, Sun and Chen, 1985
- ▲ Hexane/Mesitylene, Sun and Chen, 1985
- ● Hexane/p-Xylene, Chen et. al., 1985
- ▦ Hexane/Toluene, Chen et. al., 1985

X-axis: Molar Volume (ml/mol)

Y-axis: $D_{12}*10^9$ (m^2/s)