FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I.   Objectives for the Second Quarter, Year 4:

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

Our objective in this quarter was to develop an equation 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*. To accomplish this task we developed a correlation between the molecular dynamics simulations and semi-empirical correlation. A DEC alpha station was purchased for aid in this endevor. With the new workstation the theory can be fully checked to a high degree of accuracy in a reasonable amount of time.

II.   Accomplishments and Problems, Second Quarter, Year 4

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

The binary diffusion coefficient D_{12}, using the rough hard sphere theory, can be approximated in terms of the smooth hard sphere diffusivity by:

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

This can be rewritten as:

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

In the above equation A_{12} is the translational rotational couplong parameter, the term in parenthesis is a ratio of smooth hard spheres to enskog diffsuivities obtained by molecular dynamics simulations, and $D_{12,E}$ is the enskog dense gas diffusivity. The Enskog dense gas theory is well developed and the equation is:

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

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:

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

The rough hard spheres equation then becomes:

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

From molecular dynamics simulations, it is shown that the smooth hard sphere diffusivity to Enskog diffusivity ratio is a function of three ratios, molecular weight, molecular size, and volume:

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

It can be further assumed that:

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

Fitting available self diffusion data in the literature to a straight line, the following relationship is obtained:

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

where a and b are constants relating to the slope and intercept. Chen et al. (1982) and Matthews and Akgerman (1987) were then able to reduce the rough hard spheres equation (equation 5) to the following functionality:

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

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 similar approach to fit self diffusion data in supercritical fluids

using available molecular dynamics simulation data in the self diffusion regime. This yielded the non-linear equation of:

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

This allows 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 data on infinite dilution diffusion coefficients in supercritical fluids. Self diffusion of similar species, on the other hand, can be predicted by equation (11). Therefore one can assume that a form similar to equation (11) would be sufficient to predict infinite dilution diffusion coefficients in supercritical fluids data. Therefore we start with the general equation:

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

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 functionality's. 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. 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.

Figure 1 shows that the functionality of α is an absolute. The curves shown are a sample of results from fitting available molecular dynamics simulation results for over 350 systems. The result of the fit shows that:

$$\frac{V}{V_o}\left[\frac{D_{12,SHS}}{D_{12,E}}\right]_{MD}\frac{1}{g(\sigma_{12})} = a\left[\left(\frac{V}{V_o}\right)^{\alpha-\frac{1}{3}} - b\right] \tag{15}$$

where b is respresented by Figure 2. This gives a beginning of the simulation results and adds to the accuracy of our predictions. With more knowledge of the beta parameter a full correlation can be developed.

III.   Plans for the Third Quarter, Year 4:

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

We will attempt to find a model for the β parameter 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. The dependency of this parameter on the solvent/solute interactions will be fully analyzed and a correlation will be developed to predict the functionality.

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Figure 1. Functionality of Molecular Dynamics Simulation

$R^2 = 0.9925$

$R^2 = 0.9982$

$R^2 = 0.9896$

$R^2 = 0.9996$

$R^2 = 0.9948$

y-axis: $V/V_o \ 1/g(\sigma_{12}) \ (D_{12,SHS}/D_{12,E})_{MD}$

x-axis: $(V/V_o)^{((\sigma2/\sigma1) - 1/3)}$
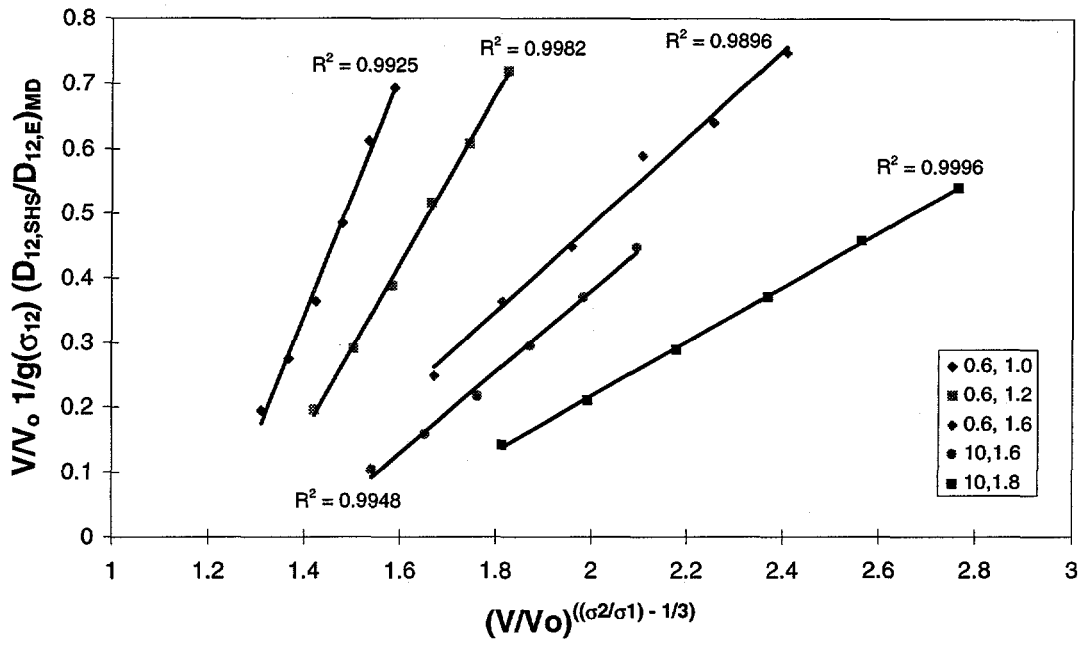
Legend:
- 0.6, 1.0
- 0.6, 1.2
- 0.6, 1.6
- 10, 1.6
- 10, 1.8

Figure 2. Functionality of b

y-axis: $b*(M1/M2)^{(-0.03587)}$

x-axis: $\sigma1/\sigma2$