FISCHER TROPSCH SYNTHESIS IN SUPERCritical FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT
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Principal Investigators
Aydin AKGERMAN
Dragomir B. BUKUR

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

Organization
Texas Engineering Experiment Station
308 Wisenbaker Engineering Research Center
College Station, TX 77843-3124

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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:

$$D_{12} = D_{12,\text{RHS}} = A_{12} D_{12,\text{SHS}} \quad (0 < A_{12} \leq 1)$$  \hspace{1cm} (1)

In this equation $D_{12,\text{RHS}}$ 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:

$$D_{12,\text{RHS}} = A_{12} \left( \frac{D_{12,\text{RHS}}}{D_{12,E}} \right)_{\text{MD}} D_{12,E} \quad (0 < A_{12} \leq 1)$$  \hspace{1cm} (2)

Here $D_{12,E}$ is the Enskog Diffusivity for gases and the ratio $(D_{12,\text{RHS}}/D_{12,E})_{\text{MD}}$ 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:

$$D_{12,E} = \frac{D_{12,\text{HSG}}}{g(\sigma_{12})}$$  \hspace{1cm} (3)

The term $D_{12,\text{HSG}}$ 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:
The rough hard spheres diffusivity is then given by:

\[
D_{12,\text{RSH}} = \frac{3}{8n_2\sigma_{12}^2} \left[ \frac{kT}{2\pi m_1 m_2} \right] \left[ \frac{1}{g(\sigma_{12})} \right] \frac{D_{12,\text{RSH}}}{D_{12,E}} A_{12}
\]

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

\[
\left( \frac{D_{12,\text{RSH}}}{D_{12,E}} \right)_{MD} = F \left( \frac{m_1}{m_2}, \frac{\sigma_1}{\sigma_2}, \frac{V}{V_o} \right)
\]

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

\[
\frac{V}{V_o} \left( \frac{D_{12,\text{RSH}}}{D_{12,E}} \right)_{MD} \frac{1}{g(\sigma_{12})} = \frac{V}{V_o} \left( \frac{D_{22,\text{RSH}}}{D_{22,E}} \right)_{MD} \frac{1}{g(\sigma_{22})}
\]

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

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

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

\[
D_{12} = \beta \sqrt{T} (V - V_o)
\]

where \( \beta \) 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 for supercritical fluids and obtained a similar relationship:
This allowed for equation (9) to be represented as:

\[ D_{12} = \beta \sqrt{\frac{2}{V^2 - 1.271V_o^2}} \]  

where the value of 2.19 is lumped into the \( \beta \) 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 similar to equation (11) can be posrulated to predict binary diffusion coefficient data.

\[ D_{12} = \beta \sqrt{T \left(V^2 - \frac{\sigma^2}{m_1} \right)} \]  

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

\[ \beta = f\left(\frac{m_1}{m_2}\right) \]  
\[ \alpha = f\left(\frac{\sigma_1}{\sigma_2}\right) = \frac{\sigma_2 - \frac{1}{3}}{\sigma_1} \]  

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 \( \alpha \) 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 \( \beta \). We have used the data we have taken and reported through the course of this project and additional data summarized below and correlated \( \beta \) 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 \( \beta \) were then fit by a non-linear regression to express the correlation as:
\[ \beta = \left( 0.05 \left( \frac{m_1}{m_2} \right)^{1.8856} \right) \cdot 10^{-9} \]  

(15)

This follows theory since it was expected that \( \beta \) would be a strong function of molecular weight. Equation (15) is specific for this system of fluids and should only be used for similar 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 \( \beta \) 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 \textit{a priori} prediction of diffusion in supercritical fluids and if necessary obtain more data to verify the theoretical approach.

References:


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Table 1. Diffusion Coefficients of 1-Octene in Ethane

<table>
<thead>
<tr>
<th>T/K</th>
<th>P/bar</th>
<th>p/kg m(^3)</th>
<th>Molar Volume/ m(^3) mol(^{-1})</th>
<th>10(^9) D(_{12})/m(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>322</td>
<td>124.1054</td>
<td>349.9</td>
<td>85.8703</td>
<td>13.26 ± 0.625</td>
</tr>
<tr>
<td>340</td>
<td>124.1054</td>
<td>299.9</td>
<td>100.1867</td>
<td>18.52 ± 0.940</td>
</tr>
<tr>
<td>357</td>
<td>124.1054</td>
<td>249.2</td>
<td>120.5698</td>
<td>22.67 ± 0.612</td>
</tr>
<tr>
<td>378</td>
<td>124.1054</td>
<td>199.9</td>
<td>150.3052</td>
<td>31.12 ± 0.346</td>
</tr>
<tr>
<td>414</td>
<td>124.1054</td>
<td>150.5</td>
<td>199.6412</td>
<td>37.61 ± 2.515</td>
</tr>
<tr>
<td>503</td>
<td>124.1054</td>
<td>100.9</td>
<td>297.7800</td>
<td>55.49 ± 4.476</td>
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Table 2. Diffusion Coefficients of 1-Octene in Propane

<table>
<thead>
<tr>
<th>T/K</th>
<th>P/bar</th>
<th>p/kg m(^3)</th>
<th>Molar Volume/ m(^3) mol(^{-1})</th>
<th>10(^9) D(_{12})/m(^2) s(^{-1})</th>
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<tbody>
<tr>
<td>314</td>
<td>124.1054</td>
<td>500.7</td>
<td>88.0647</td>
<td>9.112 ± 0.288</td>
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<tr>
<td>354</td>
<td>124.1054</td>
<td>450.7</td>
<td>97.8345</td>
<td>11.81 ± 0.393</td>
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<tr>
<td>384</td>
<td>124.1054</td>
<td>401.1</td>
<td>109.9327</td>
<td>14.31 ± 0.746</td>
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<tr>
<td>408</td>
<td>124.1054</td>
<td>350.2</td>
<td>125.9109</td>
<td>16.29 ± 0.547</td>
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<tr>
<td>429</td>
<td>124.1054</td>
<td>300.6</td>
<td>146.6866</td>
<td>22.70 ± 0.843</td>
</tr>
<tr>
<td>453</td>
<td>124.1054</td>
<td>249.6</td>
<td>176.6587</td>
<td>26.88 ± 0.664</td>
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<tr>
<td>485</td>
<td>124.1054</td>
<td>200.6</td>
<td>219.8106</td>
<td>34.59 ± 0.640</td>
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<tr>
<td>544</td>
<td>124.1054</td>
<td>150.4</td>
<td>293.1782</td>
<td>44.88 ± 0.395</td>
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<tr>
<td>523</td>
<td>62.0527</td>
<td>73.64</td>
<td>598.7778</td>
<td>66.89 ± 1.610</td>
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<tr>
<td>533</td>
<td>62.0527</td>
<td>71.31</td>
<td>618.3425</td>
<td>68.77 ± 3.551</td>
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<tr>
<td>543</td>
<td>62.0527</td>
<td>69.18</td>
<td>637.3808</td>
<td>70.61 ± 0.451</td>
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</table>
Table 3. Diffusion Coefficients of 1-Octene in Hexane

<table>
<thead>
<tr>
<th>T/K</th>
<th>P/bar</th>
<th>p/kg m$^3$</th>
<th>Molar Volume/ m$^3$ mol$^{-1}$</th>
<th>$10^9$ D$_{12}$/m$^2$s$^{-1}$</th>
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<tbody>
<tr>
<td>483</td>
<td>124.1054</td>
<td>500.2</td>
<td>172.2711</td>
<td>13.90 ± 0.325</td>
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<td>523</td>
<td>103.4212</td>
<td>437.7</td>
<td>196.8700</td>
<td>17.50 ± 0.110</td>
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<td>523</td>
<td>82.7369</td>
<td>416.5</td>
<td>206.8908</td>
<td>18.30 ± 0.715</td>
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<tr>
<td>523</td>
<td>62.0527</td>
<td>381.6</td>
<td>225.8124</td>
<td>21.20 ± 1.521</td>
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<tr>
<td>523</td>
<td>44.8158</td>
<td>312.1</td>
<td>276.0974</td>
<td>26.70 ± 2.336</td>
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<tr>
<td>563</td>
<td>62.0527</td>
<td>257.2</td>
<td>335.0311</td>
<td>35.00 ± 2.755</td>
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<tr>
<td>563</td>
<td>44.8158</td>
<td>149.8</td>
<td>375.2336</td>
<td>57.10 ± 3.145</td>
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</tbody>
</table>
Comparison of Experimental and Predicted Diffusion Coefficients for Data in this Study

- Ethane/Octene
- Propane/Octene
- Hexane/Octene

Molar Volume (ml/mol)

\[D_{12} \times 10^9 \text{ (m}^2/\text{s)}\]
Diffusion Coefficients for n-Hexane Data in the Literature

- 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