

FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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I. Objectives for the Third Quarter, Year 4:

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

We attempted 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 solvent/solute interactions on the β parameter was analyzed and a correlation developed to predict the functionality. This allowed us to develop an empirical formula to correlate the molecular diffusion coefficient to ratios of mass, size, and density. Thus finally allowing for supercritical fluid diffusion predictions *a priori*.

II. Accomplishments and Problems, Fourth Quarter, Year 3

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

Theory

Infinite dilution molecular diffusion coefficients in liquids are readily correlated by the molecular dynamics approach employing the rough hard spheres theory of diffusion (Dymond, 1985, Dymond and Woolf, 1982, Easteal and Woolf, 1984a, Easteal and Woolf, 1984b, Easteal and Woolf, 1983). In molecular dynamics simulations, Newton's laws of motion are used to calculate collisions of an ensemble of particles through computer simulations. From the time correlation of this motion, the transport properties of the fluid interaction can be determined. The calculations require the mass and diameters of the particles as well as the density of the solvent. The theory is independent of the fluid state and hence should be applicable in the supercritical region as well. The rough hard spheres approach states:

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

which can be rewritten as:

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

In the above equation A_{12} is the translational-rotational coupling parameter, the term in parenthesis is the ratio of smooth hard spheres diffusivity to Enskog diffusivity obtained by molecular dynamics simulations, and $D_{12,E}$ is the Enskog dense gas diffusivity. The translational rotational coupling parameter takes into account the momentum imparted by a non-spherical particle to adjust from the smooth hard sphere diffusivities. The Enskog dense gas theory is well developed and the equation is:

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

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) from kinetic theory as:

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

Equation 1 can then be rewritten as:

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

Through the molecular dynamics simulations it is shown that:

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

Table 1 gives the molecular dynamics simulations for $(D_{12,SHS}/D_{12,E})_{MD}$ at different m_1/m_2 , σ_1/σ_2 , and V/V_o ratios (Easteal and Woolf, 1988). The available data can be correlated by:

$$\frac{V}{V_o} \left[\frac{D_{12,SHS}}{D_{12,E}} \right]_{MD} \frac{1}{g(\sigma_{12})} = a \left(\frac{V}{V_o} \right)^a - b \quad (7)$$

where a and b are constants relating to the slope and intercept of the fitted line. The value of a was determined by Akgerman et al. (1996) as

$$\alpha = f\left(\frac{\sigma_1}{\sigma_2}\right) = \frac{\sigma_2}{\sigma_1} - \frac{1}{3} \quad (8)$$

for a limited number of systems (naphthalene, phenanthrene, and hexachlorobenzene diffusion in supercritical carbon dioxide at a narrow temperature and pressure range). The same value of a was used in fitting Equation 7 to the available molecular dynamics data given in Table 1. The results for this fitting were given in the previous quarterly report and displayed again in Figure 1.

Equation 7 can be re-written as

$$\frac{V}{V_o} \left[\frac{D_{12,SHS}}{D_{12,E}} \right]_{MD} \frac{1}{g(\sigma_{12})} = a \left[\left(\frac{V}{V_o} \right)^\alpha - \frac{b}{a} \right] \quad (9)$$

When the values of b/a are plotted versus σ_1/σ_2 , they result in a set of parallel curves. These curves can be superimposed on each other and collapsed into a single relationship as shown in Figure 2 by adjusting the b/a ratio with the molecular weight ratio. The fits given in Figure 1, then, all reduce to a single line with a new adjusted constant a_1 which is a single unique constant for evaluation of the left side of the Equation 9 with an average error of less than $\pm 1.5\%$. Equation (8) reduces to the value of $a = 2/3$ for self diffusion as reported by Erkey et al. (1990). Using the known molecular diameter and the molecular weight ratios of solute (1) to solvent (2), the value of b/a can be determined from Figure 2. A simple parabolic fit of the curve in Figure 2 yields the equation:

$$b_2 = \frac{b}{a} = \left[-0.2440 \left(\frac{\sigma_2}{\sigma_1} \right)^2 + 0.8491 \left(\frac{\sigma_2}{\sigma_1} \right) + 0.6001 \right] \left(\frac{m_1}{m_2} \right)^{-0.03587} \quad (10)$$

The rough hard spheres equation could now be represented by:

$$D_{12} = \frac{3}{8n_2\sigma_{12}^2} \left[\frac{kT(m_1+m_2)}{2\pi m_1m_2} \right]^{\frac{1}{2}} \frac{V_o}{V} a_1 \left[\left(\frac{V}{V_o} \right)^\alpha - b_2 \right] A_{12} \quad (11)$$

Combining the constants in the equation and realizing that A_{12} is dependent only upon the ratio s_1/s_2 (Erkey et al., 1990), Equation (11) can be reduced to:

$$D_{12} = \beta \sqrt{T} \left(\frac{\sigma_1}{\sigma_2} \right)^\gamma \left[\frac{(m_1+m_2)}{m_1m_2} \right]^{\frac{1}{2}} \left(\frac{V_o}{\sigma_{12}^2} \right) \left[\left(\frac{V}{V_o} \right)^\alpha - b_2 \right] \quad (12)$$

Thus there are two additional constants, b and g. The values of b and g are to be determined from experimental data taken through the course of this project and presented again in Tables 2-4. We also attempted to fit these parameters from the data in the literature, however due to the scatter in the data by various investigators (Figure 3) we decided to rely on our data only.

In using Equations 8 and 12 with Figure 2 (or Equation 10) the effective hard sphere diameters of the solute and the solvent, σ_1 and σ_2 , respectively, are needed. These values are determined from the Purkait and Majumdar (1981) semi-empirical equation given by :

$$\sigma_r = 0.552803 - 0.0026776T_r \quad (13)$$

$$T_r = \frac{T}{T_c} \quad (14)$$

$$\sigma_r = \frac{\sigma}{\sigma_c} \quad (15)$$

$$\sigma_c = \left(\frac{6V_c}{\pi N} \right)^{1/3} \quad (16)$$

Results and Discussion

The constants b and g of equation 12 were fit by a non-linear regression technique and were determined as:

$$\beta = 4.486599 \cdot 10^{-29} \left[\frac{m}{s} \sqrt{\frac{g \text{ gmol}}{K}} \right] \quad (17)$$

$$\gamma = 1.7538$$

Figure 4 is prediction of the data given in Tables 2-4 using these values of b and g in Equation 10 together with Equation 8 and Figure 2. The predictions are excellent with an average absolute error of 4.01%.

An accurate measure of the density is needed for the determination of V, the solvent molar volume. Therefore, the density is critical to the accuracy of the predictions of the diffusion coefficients. Thus a modified equation of state developed by Starling (1973) was used to determine the densities at our conditions as well as checking all possible solvent densities in the literature. The solution technique utilized a trial and error computer solution for the density. With accurately known pressures

and temperatures, the equation of state is accurate to within one percent. In checking the literature, there were some areas where the density reported did not match the temperature and pressure conditions listed. Some of these points were in error up to fifteen percent. These inconsistencies were corrected prior to any analysis of the accuracy of our developed model.

Figure 5 presents data from the literature on diffusion in supercritical alkane solvents and the predictions using the same values of b and g given in Equation 17. Figure 5 does not include our data presented in Figure 4. Again the predictions are very good. The results give a prediction that is slightly higher than the experimental value but still within the error of the experimental analysis.

Encouraged with these predictions, we attempted to use the same values of b and γ given above to predict self diffusion coefficients and data on diffusion in supercritical carbon dioxide, the solvent that is used most extensively. Figure 6 shows our predictions of the data available on the self diffusion coefficient of carbon dioxide (Chen, 1983; Takahashi and Iwasaki, 1966) ethylene (Arends et al., 1981; Baker et al., 1984), toluene (Baker et al., 1985) and chlorotrifluoromethane (Harris, 1978). The predictions, with no parameters adjusted from the data, are excellent with an average absolute error of 3.64%.

III. Plans for the First Quarter, Year 4:

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

We will attempt to compile a all encompassing literature search of supercritical fluid diffusion coefficients. Using this literature the accuracy of the model will be tested for inconsistencies in outlying areas researched. If any inconsistencies arise the model will be appropriately corrected to handle the new system. More data may need to be collected in different areas for a complete survey of the model developed. When completed this will finally allow for supercritical fluid predictions *a priori* with any fluid interaction.

Table 1. Molecular Dynamics Simulation Results

V/V ₀	s ₂ /s ₁	M ₂ /M ₁	(D _{12,SHS} /D _{12,E}) _{MD}									
			0.6	0.8	1.0	1.25	1.5	2.0	3.0	5.0	7.0	10.0
1.5	1.0		0.75	0.67	0.61	0.57	0.53	0.48	0.41	0.34	0.30	0.26
	1.2		0.70	0.68	0.65	0.62	0.60	0.55	0.48	0.40	0.34	0.29
	1.4		0.77	0.72	0.69	0.65	0.62	0.58	0.52	0.44	0.39	0.35
	1.6		0.79	0.77	0.75	0.73	0.70	0.66	0.59	0.50	0.44	0.37
	1.8		0.84	0.81	0.78	0.75	0.72	0.68	0.61	0.54	0.49	0.43
	2.0		0.84	0.83	0.81	0.79	0.78	0.74	0.68	0.60	0.54	0.48
1.6	1.0		0.85	0.81	0.77	0.74	0.70	0.65	0.57	0.48	0.42	0.36
	1.2		0.84	0.81	0.79	0.76	0.73	0.68	0.61	0.51	0.45	0.39
	1.4		0.88	0.84	0.81	0.77	0.74	0.69	0.62	0.54	0.48	0.43
	1.6		0.94	0.90	0.87	0.84	0.81	0.76	0.69	0.60	0.54	0.47
	1.8		0.94	0.91	0.89	0.86	0.83	0.79	0.73	0.64	0.58	0.52
	2.0		0.92	0.91	0.90	0.88	0.86	0.82	0.77	0.69	0.63	0.57
1.7	1.0		0.93	0.90	0.87	0.84	0.80	0.75	0.66	0.55	0.48	0.41
	1.2		0.93	0.92	0.91	0.88	0.86	0.81	0.73	0.62	0.54	0.46
	1.4		0.98	0.96	0.94	0.91	0.88	0.83	0.75	0.64	0.57	0.49
	1.6		0.97	0.95	0.93	0.91	0.89	0.85	0.78	0.69	0.63	0.56
	1.8		1.03	1.00	0.98	0.95	0.92	0.88	0.81	0.73	0.66	0.60
	2.0		0.98	0.96	0.95	0.93	0.92	0.89	0.84	0.76	0.71	0.65
1.8	1.0		1.05	1.01	0.97	0.93	0.90	0.83	0.74	0.62	0.53	0.45
	1.2		1.05	1.01	0.98	0.94	0.91	0.86	0.78	0.68	0.61	0.54
	1.4		1.05	1.02	0.99	0.96	0.94	0.89	0.81	0.71	0.64	0.57
	1.6		1.09	1.04	1.01	0.97	0.95	0.90	0.83	0.74	0.69	0.63
	1.8		1.02	1.01	0.99	0.97	0.95	0.92	0.86	0.78	0.72	0.66
	2.0		1.03	1.01	0.99	0.97	0.95	0.92	0.87	0.81	0.76	0.71
1.9	1.0		1.14	1.09	1.05	1.00	0.96	0.90	0.80	0.68	0.60	0.52
	1.2		1.07	1.05	1.02	0.99	0.96	0.91	0.83	0.72	0.64	0.56
	1.4		1.06	1.05	1.03	1.01	0.98	0.94	0.87	0.77	0.69	0.62
	1.6		1.03	1.03	1.02	1.01	0.99	0.96	0.89	0.79	0.72	0.63
	1.8		1.08	1.06	1.04	1.02	1.00	0.96	0.90	0.82	0.77	0.71
	2.0		1.04	1.03	1.02	1.00	0.99	0.96	0.92	0.85	0.79	0.74
2.0	1.0		1.13	1.10	1.06	1.02	0.99	0.94	0.85	0.74	0.67	0.59
	1.2		1.11	1.10	1.08	1.06	1.04	0.99	0.91	0.79	0.71	0.62
	1.4		1.07	1.06	1.05	1.03	1.01	0.97	0.91	0.81	0.74	0.66
	1.6		1.06	1.06	1.05	1.04	1.02	0.99	0.93	0.83	0.77	0.69
	1.8		1.07	1.06	1.05	1.03	1.02	0.99	0.94	0.86	0.81	0.74
	2.0		1.03	1.05	1.05	1.04	1.04	1.02	0.97	0.89	0.83	0.76

Table 2. Diffusion Coefficients of 1-Octene in Ethane

T/K	P/bar	$r/\text{kg m}^{-3}$	Molar Volume/ $\text{m}^3 \text{mol}^{-1}$	$10^9 D_{12}/\text{m}^2\text{s}^{-1}$
322	124.1054	349.9	85.8703	16.26 ± 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 3. Diffusion Coefficients of 1-Octene in Propane

T/K	P/bar	$r/\text{kg m}^{-3}$	Molar Volume/ $\text{m}^3 \text{mol}^{-1}$	$10^9 D_{12}/\text{m}^2\text{s}^{-1}$
314	124.1054	500.7	88.0647	11.81 ± 0.288
354	124.1054	450.7	97.8345	14.31 ± 0.393
384	124.1054	401.1	109.9327	16.29 ± 0.746
408	124.1054	350.2	125.9109	22.70 ± 0.547
429	124.1054	300.6	146.6866	26.88 ± 0.843
453	124.1054	249.6	176.6587	24.59 ± 0.664
485	124.1054	200.6	219.8106	44.88 ± 0.640
544	124.1054	150.4	293.1782	54.65 ± 0.395
523	62.0527	73.64	598.7778	86.89 ± 1.610
533	62.0527	71.31	618.3425	88.77 ± 3.551
543	62.0527	69.18	637.3808	90.61 ± 0.451

Table 4. Diffusion Coefficients of 1-Octene in Hexane

T/K	P/bar	$\rho/\text{kg m}^{-3}$	Molar Volume/ $\text{m}^3 \text{mol}^{-1}$	$10^9 D_{12}/\text{m}^2\text{s}^{-1}$
483	124.1054	500.2	172.2711	18.50 ± 0.325
523	103.4212	437.7	196.8700	22.50 ± 0.110
523	82.7369	416.5	206.8908	26.22 ± 0.715
523	62.0527	381.6	225.8124	29.70 ± 1.521
523	44.8158	312.1	276.0974	38.97 ± 2.336
563	62.0527	257.2	335.0311	53.00 ± 2.755
563	44.8158	149.8	575.2336	82.10 ± 3.145

NOTATION

A_{ij}	=	translational rotational coupling parameter
D	=	diffusion coefficient
D_{ij}	=	mutual diffusion coefficient
$g(s_{ij})$	=	radial distribution function
k	=	Boltzmann constant
m	=	mass of single molecule
n	=	number density
T	=	absolute temperature
V	=	molar volume
V_D	=	molar volume scaling
V_0	=	close-packed hard sphere volume
a	=	fitting parameter for self diffusion
b	=	fitting parameter for self diffusion

Subscripts

1	=	solute
2	=	solvent
E	=	Enskog
HSG	=	hard spheres gas
MD	=	molecular dynamics
RHS	=	rough hard spheres
SHS	=	soft hard spheres

Greek Letters

s	=	diameter
s_{ij}	=	average diameter
a	=	exponential parameter, defined by equation (8)
b	=	slope parameter, defined by equation (11)
g	=	V/V_0 relationship parameter, defined by equation (11)

Figure 1. Correlation of Molecular Dynamics Simulation Data given in Table 1.

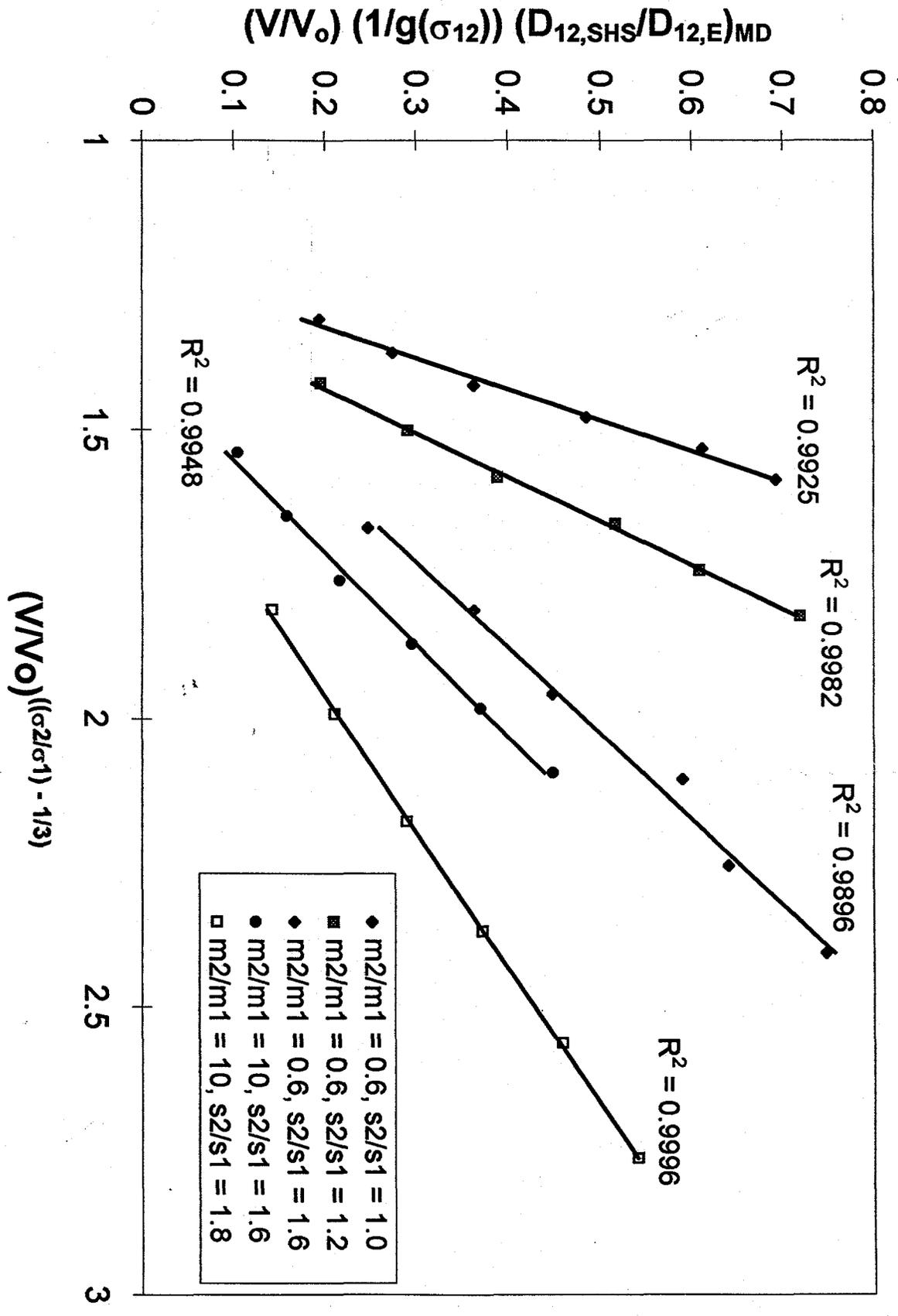


Figure 2. Functionality for b_2 (Equation 10)

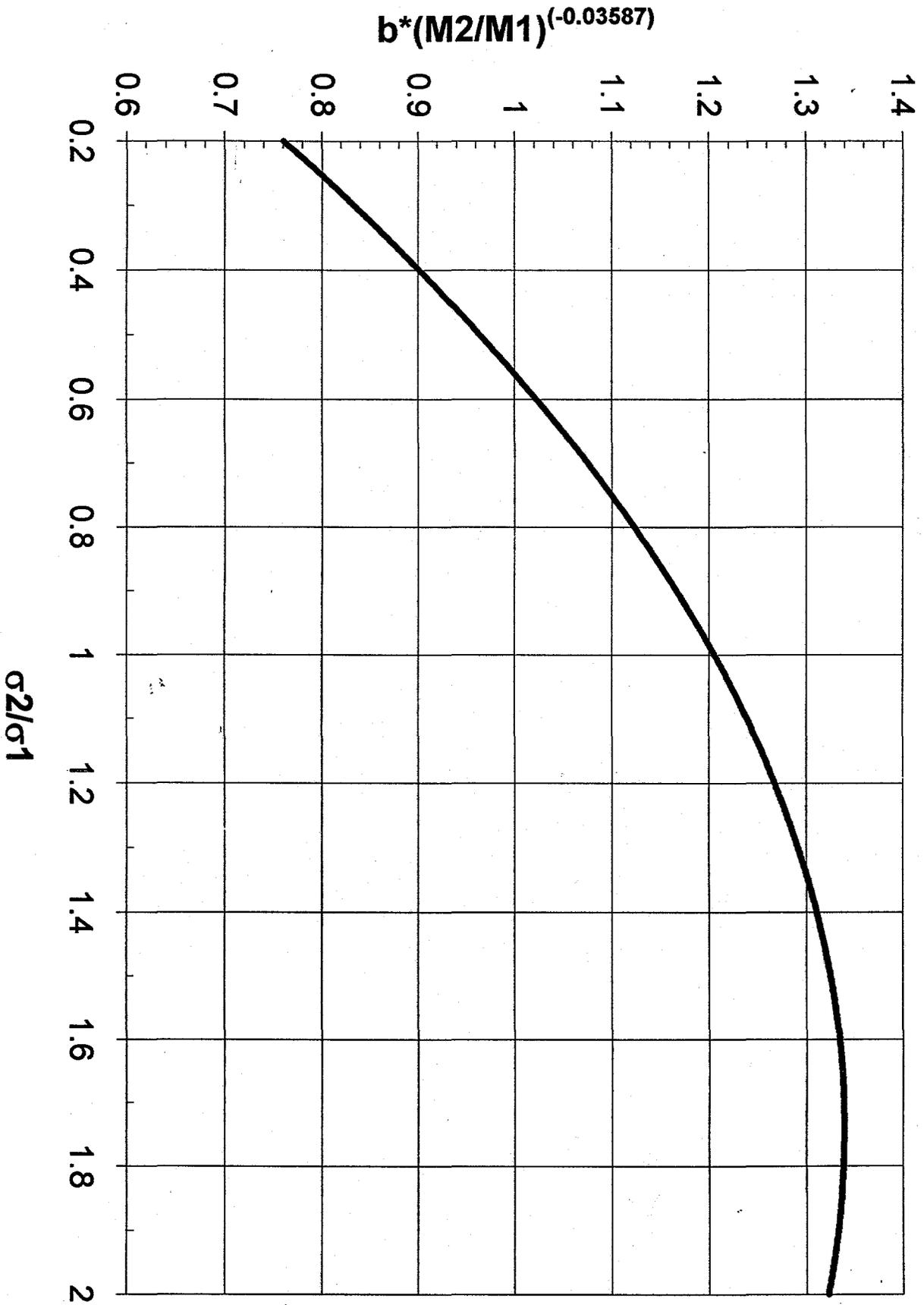


Figure 3. Data on Naphthalene Diffusion in Supercritical Carbon Dioxide Reported in the Literature

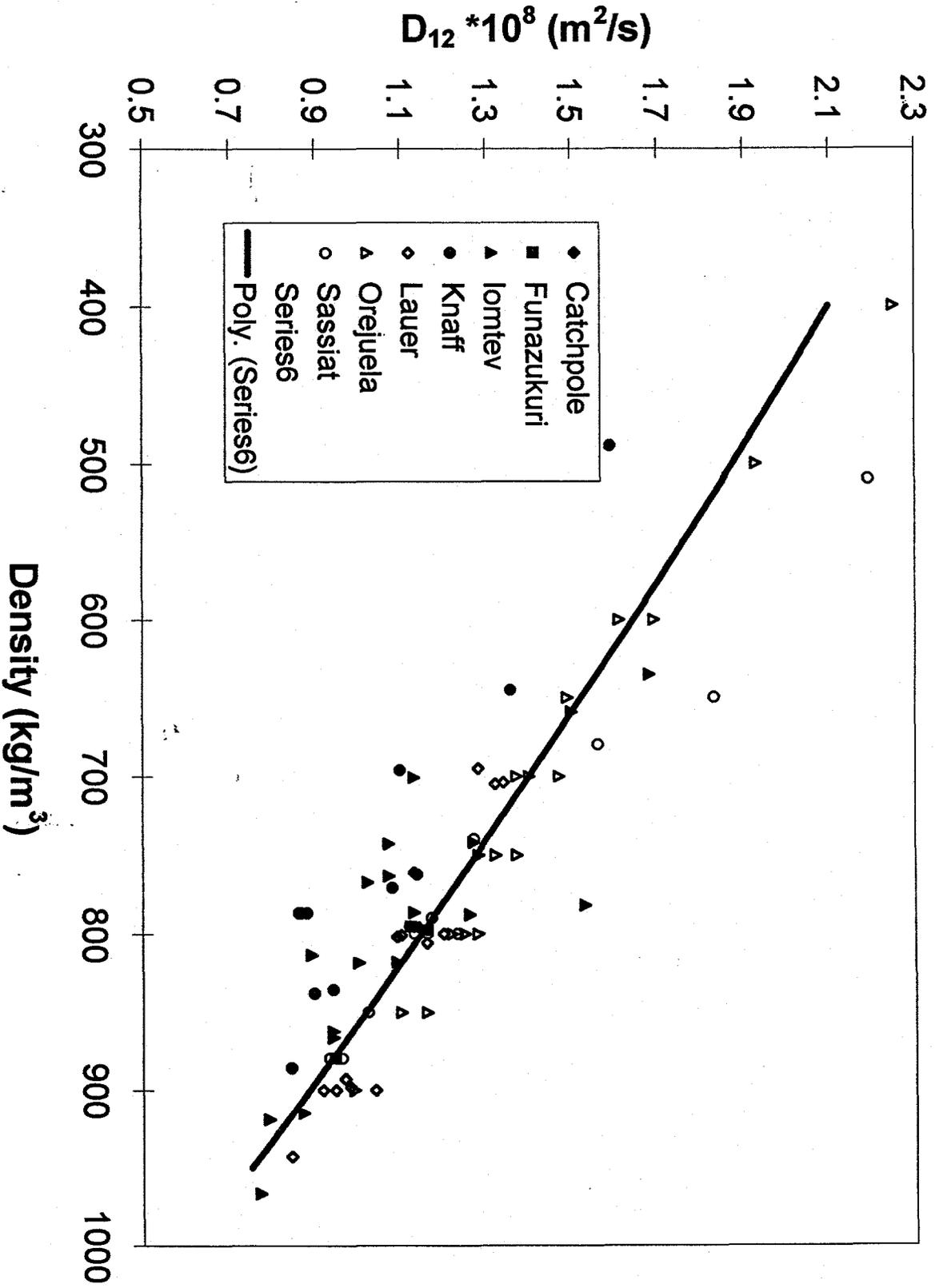


Figure 4. Comparison of Experimental and Predicted Diffusion Coefficients for Data Presented in this Study (Tables 2-4)

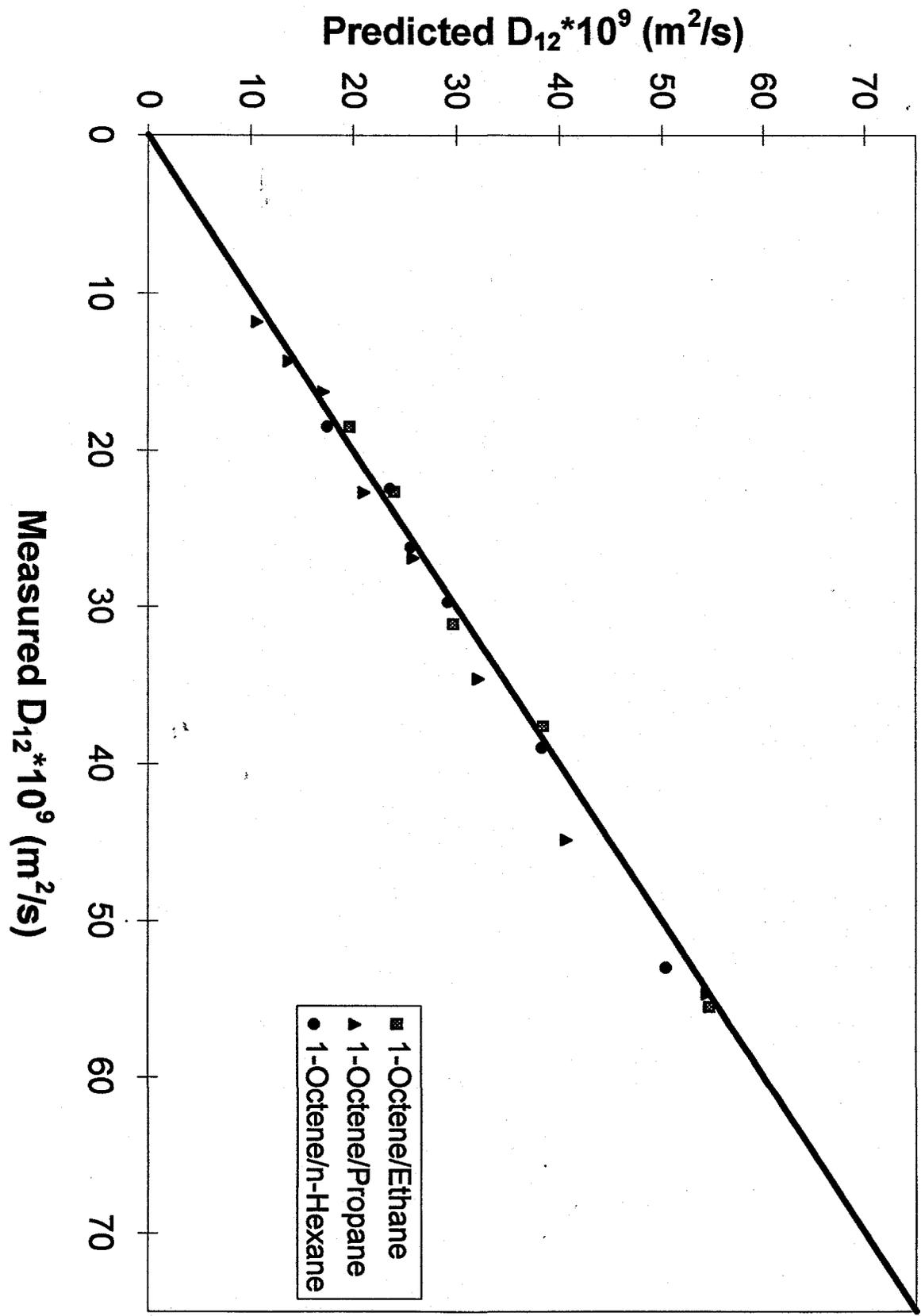


Figure 5. Comparison of Experimental and Predicted Values of Diffusion Coefficients of Various Solutes in Alkanes

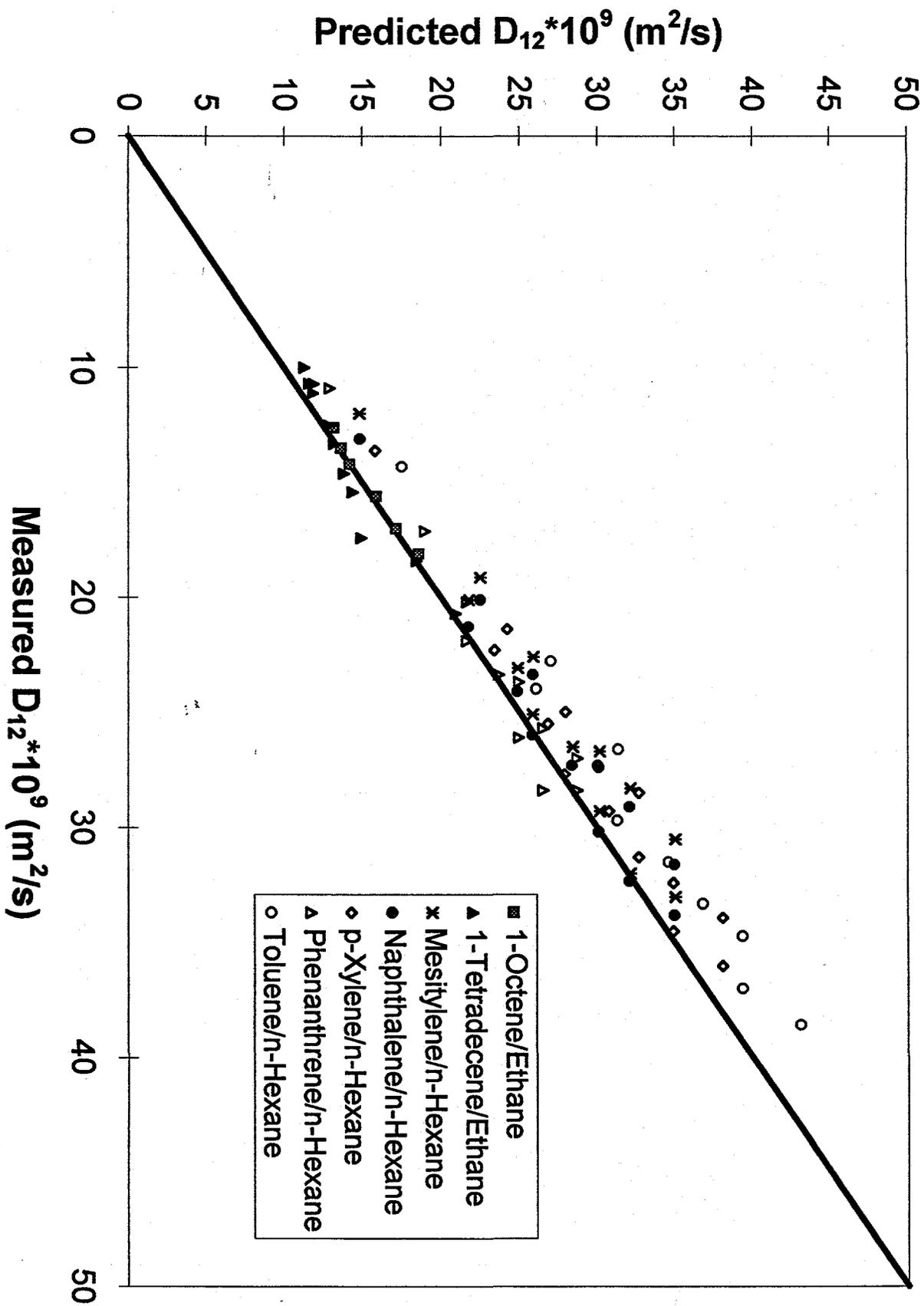
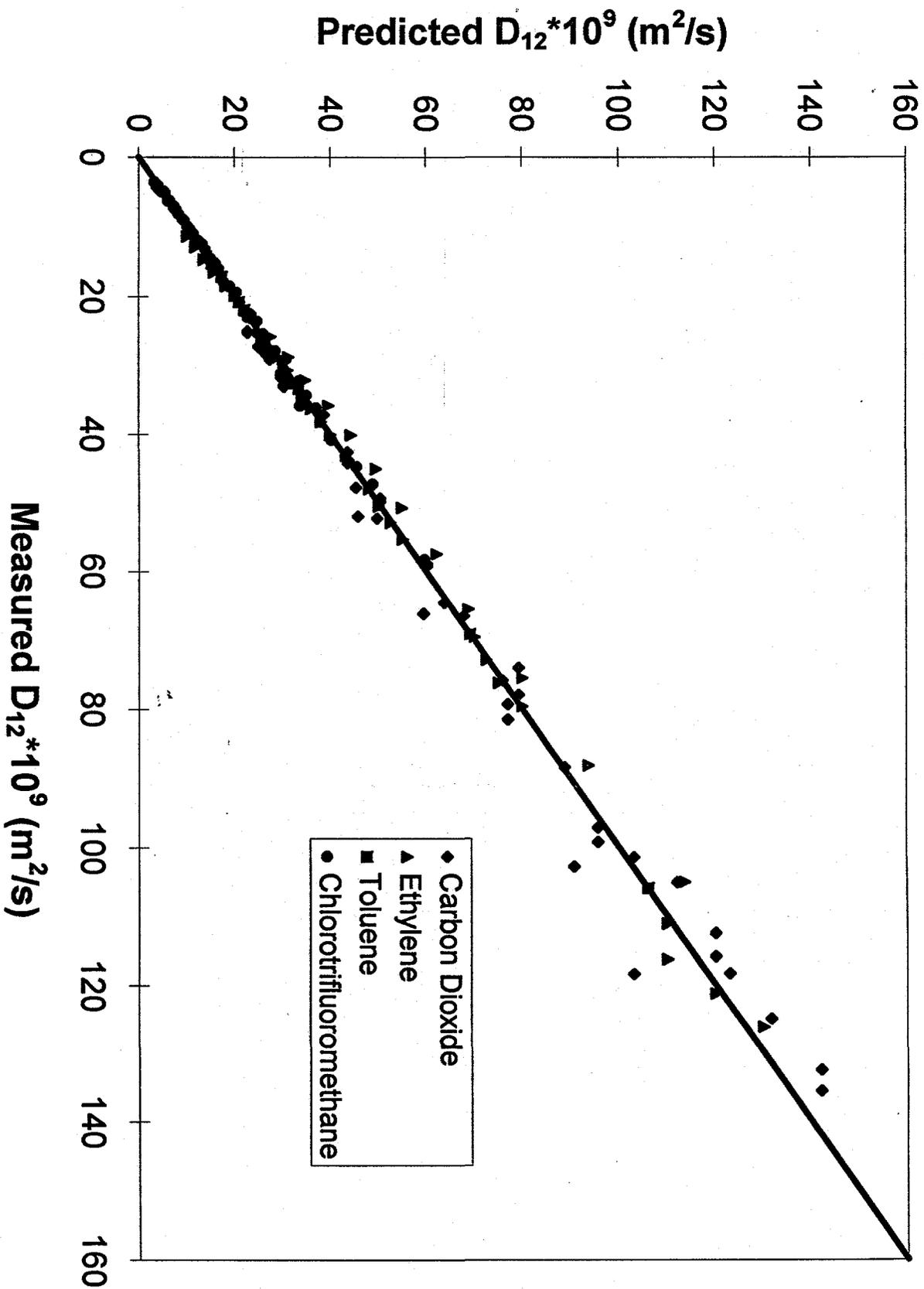


Figure 6. Parity Plot for Self Diffusion of Supercritical Carbon Dioxide, Ethylene, Toluene, and Chlorotrifluoromethane



LITERATURE CITED

- Akgerman, A., Erkey, C., and Orejula, M., "Limiting Diffusion Coefficients of Heavy Molecular Weight Organic Contaminants in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **35**, 911 (1996).
- Alizadeh, A. A., Nieto de Castro, C. A., and Wakeham, W. A., "The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements," *Int. J. Thermophys.*, **1**, 243 (1980).
- Arends, B., Prins, K.O., and Trappeniers, N.J., "Self-Diffusion in Gaseous and Liquid Ethylene," *Physica*, **107A**, 307 (1981).
- Baker, E.S., Brown, D.R., and Jonas, J., "Self-Diffusion in Compressed Supercritical Ethylene," *J. Phys. Chem.*, **88**, 5425, (1984).
- Baker, E. S., Brown, D. R., Lamb, D. M., and Jonas, J., "Self-Diffusion in Compressed Supercritical Toluene-d₈," *J. Chem. Eng. Data*, **30**, 141, (1985).
- Chen, H.C., Sun, C.K., Chen, S.H. "Hard Sphere Treatment of Binary Diffusion in Liquid at High Dilution to the Critical Temperature," *J. Chem. Phys.*, **82**, 2052 (1985).
- Dymond, J. H. "Hard-Sphere Theories of Transport Properties," *Chem. Soc. Rev.*, **3**, 317 (1985).
- Dymond, J. H., and Woolf, L. A., "Tracer Diffusion of Organic Solutes in n-Hexane at Pressures up to 400 MPa," *J. Chem. Soc., Faraday Trans.*, **78**, 991 (1982).
- Eaton, A., Bukur, D. B., and Akgerman, A. , "Molecular Diffusion Coefficients and Effective Diffusivities of 1-Octene in Supercritical Ethane in Relation to Fischer-Tropsch Synthesis," *J. Chem. Eng. Data*, **40**, 1293 (1995).
- Easteal, A. J., Woolf, L. A., and Jolly, D. L., "Self Diffusion in a Dense Hard Sphere Fluid: A Molecular Dynamics Simulation," *Physica*, **121A**, 286 (1983).
- Easteal, A. J., and Woolf, L. A., "Diffusion in Mixtures of Hard Spheres at Liquid Densities: A Comparison of Molecular Dynamics and Experimental Data in Equimolar Systems," *Chem Phys.*, **88**, 101 (1984a).
- Easteal, A. J., and Woolf, L. A., "On the Number Dependence of Hard-Spheres Diffusion of Coefficients from Molecular Dynamics Simulations," *Physica*, **127A**, 344 (1984b).

Easteal, A. J., and Woolf, L. A., "Development in the Hard Sphere Model for Self-Diffusion and Shear Viscosity. I. Methane as a Model Hard Sphere Fluid," *Physica*, **124B**, 182 (1984c).

Easteal, A. J., and Woolf, L. A., "Molecular Dynamics Simulation Results," *unpublished transaction*, (1988)

Erkey, C., and Akgerman, A., "Chromatography Theory: Application To Supercritical Fluid Extraction," *AIChE Journal*, **36**, 1715 (1990).

Erkey, C., Gadalla, H., and Akgerman, A., "Application of Rough Hard Sphere Theory to Diffusion in Supercritical Fluids," *Journal of Supercritical Fluids*, **3**, 180 (1990).

Harris, K. R., "The Density Dependence of the Self-Diffusion Coefficient of Chlorotrifluoromethane Near the Critical Temperature," *Physica.*, **93A**, 593 (1978).

Starling, K. E., *Fluid Thermodynamic Properties for Light Petroleum Systems*, Gulf Publishing Company, Houston, TX (1973).

Takahashi, S., and Hiroji I. , "The Diffusion of Gases at High Pressures. I. The Self-Diffusion Coefficient of Carbon Dioxide," *Bull. Chem. Soc. Japan*, **39**, 2105 (1966).