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FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

July 1, 1996 - September 30, 1996

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I. Objectives for the Fourth Quarter, Year 4:

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

Completion of the project by developing an equation to predict diffusion coefficients in supercritical fluids and evaluating the equation our as well as literature data.

II. Accomplishments and Problems, Fourth Quarter, Year 4

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

The key equations for the model prediction base are:

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

$$\alpha = f \left(\frac{\sigma_1}{\sigma_2} \right) = \frac{\sigma_2}{\sigma_1} - \frac{1}{3} \quad (2)$$

$$b_2 = \frac{b}{a} = \left[-0.2440 \left(\frac{\sigma_2}{\sigma_1} \right)^2 + 0.8491 \left(\frac{\sigma_2}{\sigma_1} \right) + 0.6001 \right] \left(\frac{m_1}{m_2} \right)^{-0.03587} \quad (3)$$

$$\beta = 4.486599 \cdot 10^{-29} \left[\frac{m}{s} \sqrt{\frac{g \text{ gmol}}{K}} \right] \quad (4)$$

$$\gamma = 1.7538$$

As proposed in the previous quarterly report, these equations should allow for the prediction of any fluid interaction in the supercritical regime.

Figures 1, 2 and 3 are predictions of diffusion coefficients of various solutes in supercritical carbon dioxide. Some of the scatter in the predictions is due to the scatter in the data obtained by different investigators for the same system at the same conditions. Figures 4, 5, 6, 7, and 8 show predictions of diffusion of various solutes in supercritical alcohols, 2,3-dimethylbutane, and sulphurhexafluoride, respectively. In general, the predictions are somewhat high for diffusion in 2,3-dimethylbutane, and good for diffusion in alcohols and sulphurhexafluoride. In all of these cases (Figures 1-8) the predictions are within the range of errors of these sets of experimental data. However, for some systems, the predictions fail by more than 35%.

The available literature data on diffusion in supercritical fluids, and very high density, near critical fluids, and their predictions using Equations 1, 2, 3, and 4 are presented in Tables 1 and 2 again without any data reduction. These Tables contain, to the best of our knowledge, all the published data in the literature on infinite dilution diffusion coefficient measurements in supercritical and very high density fluids. It should be noted that we have not performed any data reduction and evaluated all the data in the literature as measured and reported correct. This was done on purpose in order to correctly show the range of applicability of the proposed equation. Therefore, caution should be taken when attempting to use the data in these tables. The high density near critical fluids are also included to display the predictions of the proposed equation in that range as well. The tables are broken up into two classifications. It seemed that there was a definite differentiation between predictions of diffusivities of compounds with known critical constants (T_c and V_c) versus predictions of diffusivities of compounds with estimated critical constants. Therefore, the two tables represent data for systems for which the critical constants are available from the literature (experimentally determined) and those for which these constants have to be predicted by group contribution techniques. The uncertainties involved in evaluating the critical constants introduces significant error in the prediction of the diffusion coefficient due to the fact that they are vital in the determination of the molecular diameters. The critical constants (T_c and V_c), if they are not available from the literature data, were determined by the group contribution methods of Joback, Ambrose, and Fedor (Reid and Prausnitz, 1987). To determine the critical temperature of compounds for which the boiling point was unavailable or uncertain, the method of Fedor was used. For compounds for which the boiling point was known and accurate, the method of Joback was used. Reid and Prausnitz (1987) state that this is the most accurate way of determining the critical temperatures with known values of the boiling point. The critical volumes, in all cases, were also determined by the method of Joback, due to the reference of accuracy by Reid and Prausnitz (1987). The method of Ambrose was used as a scale to determine if there were any predictions that could be considered unrealistic. Ambrose's method predicted the values of the critical constants within thirty percent of the other methods utilized. Since this is the typical accuracy of the group contribution methods for compound of this structure in determining the critical constants, the values were accepted and predictions were completed on these points.

The average absolute error for all points in Table 2 is 22.6%. In order to demonstrate the effect of the uncertainties in critical properties on the prediction of diffusion, we introduced 10 - 30% error (increase) to the critical temperature and volume of 1-octene (the solute) and calculated the diffusion coefficients with these new hypothetical critical constants. Table 3 shows the random increase in the error in predictions of diffusion coefficients due to this increase in critical constants. Therefore, the prediction technique presented here necessitates accurate values for the critical temperature and the volume of the solvent and solute, or accurate values for the effective hard sphere diameters.

The overall average deviation of the predictions for both tables (including 101 systems and over 1548 data points) is 15.08% and the predictions are excellent to acceptable for most solvent/solute pairs, including the polar compounds. The average absolute error for the systems in Table 1 is 9.62%. This average does not include four sets of data on diffusion of ketones in carbon dioxide, for which the average error was 37.82%. Since the predictions on these systems

were not good and the literature data seemed to be taken in a well defined manner, we have repeated the ketone experiments, using representative areas of the data including both end points and two additional data points in the middle, and measured diffusion coefficients of ketones (3-pentanone, 3-heptanone, and 2-heptanone) in supercritical carbon dioxide to compare our findings to the data in the literature. We obtained experimental values within $\pm 10\%$ of the literature data. However, we observed that the Taylor dispersion peaks obtained were both non-Gaussian (exhibiting wider dispersion) and skewed with a tail, indicating that these compounds do adsorb on the 316 stainless steel diffusion column (or somewhere else in the system). Figure 9 is a representative data set comparing the experimental data with the predicted response curve. The experimental pulse-response data will always result in a value for the diffusion coefficient, but it is imperative to make sure that the response curve is Gaussian. A non-Gaussian curve with a tail implies adsorption and the Aris/Taylor analysis of Taylor dispersion is invalidated (Alizadeh et al., 1980). Therefore, we believe that the data reported on these compounds are possibly in error as well since the authors also used a 316 stainless steel diffusion column. In addition, although our predictions of the diffusion coefficients of acid esters in carbon dioxide were quite good, a closer analysis indicated that the trend in the data and predictions were skewed. Similarly, we measured diffusion coefficients of butyric acid ethyl ester, caprylic acid ethyl ester, maristic acid ethyl ester and stearic acid ethyl ester in supercritical carbon dioxide at conditions reported in the literature. Our experimental data again matched the literature within $\pm 10\%$. However, we again observed that the Taylor dispersion peaks were non-Gaussian, more like a square peak (a peak with a flattened top portion and larger dispersion) with a tail. Figure 10 is a plot of typical response with the fitted theoretical curve which lies within the experimental peak matching the maximum but neither the beginning and the end nor the steepness. This also indicates adsorption or other phenomena that invalidates Aris/Taylor analysis. Therefore, we believe that the data on diffusion of acid esters should also be used with caution as well.

III. Plans for the First Quarter, Year 5:

The project is completed and it is terminated on September 30, 1996. We are in process of completing our draft of the final report and expect to submit it very soon for approval. Upon approval the recommended changes will be completed and desired number of copies of the final report will be mailed.

Table 1. Comparison of model to literature data for systems with known critical constants (T_c and V_c)

Solvent	Solute	Temperature Range (K)	Density Range (kg/m^3)	Average Absolute Percent Error	Citations
Sulphurhexafluoride	Naphthalene	318.2-328.2	1108.5-1489.71	13.74	25
	1,3,5-Trimethylbenzene	328	300-1400	18.70	11
	1,4-Dimethylbenzene	283.2-338.2	300-1650	16.07	11
	Benzene	328	300-1400	24.32	11
	Methylbenzene	328	300-1400	19.21	11
	Tetrachloromethane	328	300-1400	28.80	11
Ethylene	Carbon Dioxide	298.2-348.2	11.04-342.16	7.87	29
	Ethylene	298.2-398.2	125-580.1	3.76	31,32
Chlorotrifluoromethane	Chlorotrifluoromethane	303.2-348.2	351.03-1807.94	3.11	34
Toluene	Toluene	573.2-723.2	200.49-717.26	0.45	33
2,3-Dimethylbutane	Benzene	523.2-548.2	392.72-523.35	21.12	20
	Naphthalene	523.2-548.2	392.72-523.35	7.52	20
	Phenanthrene	523.2-548.2	392.72-523.35	4.85	20
	Toluene	523.2-548.2	392.72-523.35	14.00	20
Carbon Dioxide	Acetone	303.2-333.2	510-880	5.28	18
	Naphthalene	288.3-351.2	325.6-1112.28	12.42	2,7,8,9, 10,12,15, 17,18,26
	Phenanthrene	303.2-333.2	325.61-900	14.87	15,17,18,
	1,3,5-Trimethylbenzene	308.2-333.2	510-800	5.66	18,28
	Benzene	303.2-333.2	280-800	6.24	1,4,7,8, 12,18,19, 28
	Ethylbenzene	313.2-333.2	607.1-911.2	8.91	1,19
	Hexachlorobenzene	298-328	400-900	10.71	15,17
	i-Propylbenzene	313.2-333.2	607.1-936.1	8.44	1,19
	m-Xylene	313.2	795.57	10.73	1
	Mesitylene	313.2	795.57	8.40	1
	n-Propylbenzene	308.2-333.2	607.1-800	10.09	1,19,28
	o-Xylene	313.2	795.57	11.58	1
	p-Xylene	313.2	795.57	13.12	1
	Pentachlorophenol	308-328	400-900	3.34	15,17
	Toluene	313.2-333.2	607.1-936.1	6.53	1,19
	Ethylene	298.2-348.2	92.22-789.44	22.62	29

	Carbon Dioxide	308.2-373.2	158-757	5.29	4,30
Ethane	1-Octene	296.2-322.2	308.4-399.1	1.64	16
	1-Tetradecene	293.2-322.2	308-404	7.66	16
n-Hexane	Benzene	273.2-533.3	346-677	19.42	3,22
	Mesitylene	333.2-533.3	346-622	10.22	22
	Naphthalene	333.2-533.3	346-622	6.12	22
	p-Xylene	333.2-533.3	346-622	7.90	22
	Phenanthrene	333.2-533.3	346-622	5.15	22
	Toluene	333.2-533.3	346-622	12.11	22
Ethanol	Benzene	313.2-554	398-772	11.71	21
	Mesitylene	473.4-554	398-567	12.92	21
	Naphthalene	473.4-554	398-567	15.93	21
	Phenanthrene	473.4-554	398-567	15.10	21
	Toluene	473.4-554	398-557	14.14	21
2-Propanol	Benzene	473.2-536	417-569	7.35	27
	n-decane	473.2-536	417-569	10.48	27
	n-tetradecane	473.2-536	417-569	6.19	27
	Naphthalene	473.2-536	417-569	8.46	27
	Phenanthrene	473.2-536	417-569	6.43	27
	Toluene	473.2-536	417-569	8.21	27
			Average:	9.62	
Carbon Dioxide	2-Butanone	314.5	531-812	35.81	5
	2-Pentanone	314.5	531-812	37.22	5
	2-Propanone	314.5	619-792	26.01	5
	3-Pentanone	314.5	586-812	43.02	5,24
			Average:	37.82	

Citations: 1) Bueno, 1993; 2) Catchpole, 1994; 3) Chen et al., 1985; 4) Chen, S.H., 1983; 5) Dahmen, 1990a; 6) Funazukuri, 1991; 7) Funazukuri, 1992; 8) Funazukuri, 1989; 9) Iometev, 1964; 10) Knaff, 1987; 11) Kopner, 1987; 12) Lauer, 1983; 13) Liong, 1991; 14) Liong, 1992; 15) Madras *et al.*, 1994; 16) Noel, 1994; 17) Orejula, 1994; 18) Sassiati, 1987; 19) Suarez, 1993; 20) Sun and Chen, 1985a; 21) Sun and Chen, 1986; 22) Sun and Chen, 1985b; 23) Well, 1992; 24) Dahmen, 1990b; 25) Debenedetti, 1986; 26) Lamb, 1989; 27) Sun and Chen, 1987; 28) Swaid, 1979; 29) Takahashi and Hongo, 1982; 30) Takahashi and Hiroji, 1966; 31) Arends *et al.*, 1981; 32) Baker, 1984; 33) Baker, 1985; 34) Harris, 1978.

Table 2. Comparison of model to literature data for systems for which the critical constants are predicted by group contribution

Solvent	Solute	Temperature Range (K)	Density Range (kg/m ³)	Average Absolute Percent Error	Citations
Sulphurhexafluoride	Benzoic Acid	328.2-338.2	917.2-1400.6	46.23	25
Carbon Dioxide	2,2,4,4-Tetramethyl-3-Pentanone	313.5	619-792	39.60	5
	2,4-Dimethyl-3-Pentanone	313.5	619-792	39.60	5
	2-Heptanone	314.5	531-812	39.07	5
	2-Nonanone	314.5	586-812	37.18	5
	4-Heptanone	314.5	619-792	40.91	5
	5-Nonanone	314.5	586-812	45.03	5,24
	6-Undecanone	314.5	586-812	35.95	5
	3-Heptanone	314	596-812	55.12	24
	Behenic Acid Ethyl Ester	308-318	600-850	20.37	13,14
	Butric Acid Ethyl Ester	308-318	600-850	11.00	14
	Capric Acid Ethyl Ester	308-318	600-850	10.57	14
	Caprylic Acid Ethyl Ester	308-318	600-850	10.03	14
	cis-11-Eicosenoic Acid Methyl Ester	313	795.57-879.97	30.40	7
	Docosahexaenoic Acid Ethyl Ester	308-318	600-850	15.82	13,14
	Docosahexaenoic Acid Methyl Ester	308-318	600-850	15.47	6,13,14
	Eicosapentaenoic Acid Ethyl Ester	308-318	600-850	15.28	6,13
	Eicosapentaenoic Acid Methyl Ester	308-318	600-850	15.65	14
	Erucic Acid Methyl Ester	313	795.57-879.97	34.02	7
	Linoleic Acid Methyl Ester	308.2-328.2	739-929	21.28	6
	Myristic Acid Ethyl Ester	308-318	600-850	11.67	14
	Myristoleic Acid Methyl Ester	313	795.57-879.97	19.13	7
	Nervonic Acid Methyl Ester	313.2	792.3	32.37	6
	Oleic Acid Methyl Ester	313.2	792.3	20.07	6

Palmitoleic Acid Ethyl Ester	308-318	600-850	13.66	6,14	
Stearic Acid Ethyl Ester	308-318	600-850	15.01	13,14	
Benzoic Acid	298.8-318.1	537.2-858.7	13.10	2,25	
Caffeine	313.3-333.2	550.1-795.31	17.49	10,12	
Chrysene	303.2-333.2	800-880	6.87	18	
d1-Limonene	313	795.57-879.97	6.39	7	
Glycerol Trioleate	308.1	867.3-902.5	97.00	2	
Indole	313	795.57-879.97	0.75	7	
Linoleic Acid	313.5	703-812	7.34	5	
Oleic Acid	308.1-313.5	657-902.5	38.38	2,5	
Phenylacetic Acid	308.2-313.2	600-850	5.78	23	
Pyrene	303.2-333.2	650-880	12.50	18	
Squalene	313.5	703-812	5.25	5	
Stearic Acid	313.5	739-792	33.29	5	
Vanillin	308.2-318.2	600-850	9.14	23	
Vitamin A Acetate	313	795.57-879.97	32.31	7	
Vitamin E	308.1-313	795.57-902.5	40.31	7	
Vitamin K1	313	795.57-879.97	53.07	7	
Vitamin K3	313	795.57-879.97	5.71	7	
Chlorotrifluoromethane	1,3-Dibromobenzene	318.15	400-1000	40.75	11
	2-Propanone	313.15	398-956	40.37	11
	p-Xylene	318.15	400-1000	29.17	11
			Average:	22.60	

Citations: 1) Bueno, 1993; 2) Catchpole, 1994; 3) Chen et al., 1985; 4) Chen, S.H., 1983; 5) Dahmen, 1990a; 6) Funazukuri, 1991; 7) Funazukuri, 1992; 8) Funazukuri, 1989; 9) Iometev, 1964; 10) Knaff, 1987; 11) Kopner, 1987; 12) Lauer, 1983; 13) Liong, 1991; 14) Liong, 1992; 15) Madras et al., 1994; 16) Noel, 1994; 17) Orejula, 1994; 18) Sassiati, 1987; 19) Suarez, 1993; 20) Sun and Chen, 1985a; 21) Sun and Chen, 1986; 22) Sun and Chen, 1985b; 23) Well, 1992; 24) Dahmen, 1990b; 25) Debenedetti, 1986; 26) Lamb, 1989; 27) Sun and Chen, 1987; 28) Swaid, 1979; 29) Takahashi and Hongo, 1982; 30) Takahashi and Hiroji, 1966; 31) Arends *et al.*, 1981; 32) Baker, 1984; 33) Baker, 1985.

Table 3. Average errors for prediction of 1-octene diffusion in ethane with error introduced to T_c and V_c of 1-octene

							Average:
Known values of T_c and V_c	0.704	5.84	5.67	-4.63	1.97	1.60	3.40
+10% error in T_c and V_c	3.64	11.23	11.82	1.65	9.63	7.11	7.51
+20% error in T_c and V_c	8.90	17.75	19.26	9.28	19.01	17.96	15.36
+30% error in T_c and V_c	15.43	25.83	28.52	18.83	30.86	31.93	25.23
+10% error in V_c	4.10	1.64	0.900	9.47	3.83	8.00	4.66
+20% error in V_c	7.04	2.00	3.24	13.70	8.84	13.50	8.05
+30% error in V_c	9.62	5.21	6.88	17.30	13.20	18.30	11.75
+10% error in T_c	0.986	5.48	5.23	5.11	1.35	2.45	3.43
+20% error in T_c	1.22	5.17	4.87	5.50	0.834	3.14	3.46
+30% error in T_c	1.42	4.91	4.56	5.85	0.400	3.73	3.48

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
<i>E</i>	=	Enskog
<i>HSG</i>	=	hard spheres gas
<i>MD</i>	=	molecular dynamics
<i>RHS</i>	=	rough hard spheres
<i>SHS</i>	=	soft hard spheres

Greek Letters

σ	=	diameter
σ_{ij}	=	average diameter
α	=	exponential parameter, defined by equation (8)
β	=	slope parameter, defined by equation (11)
γ	=	V/V ₀ relationship parameter, defined by equation (11)

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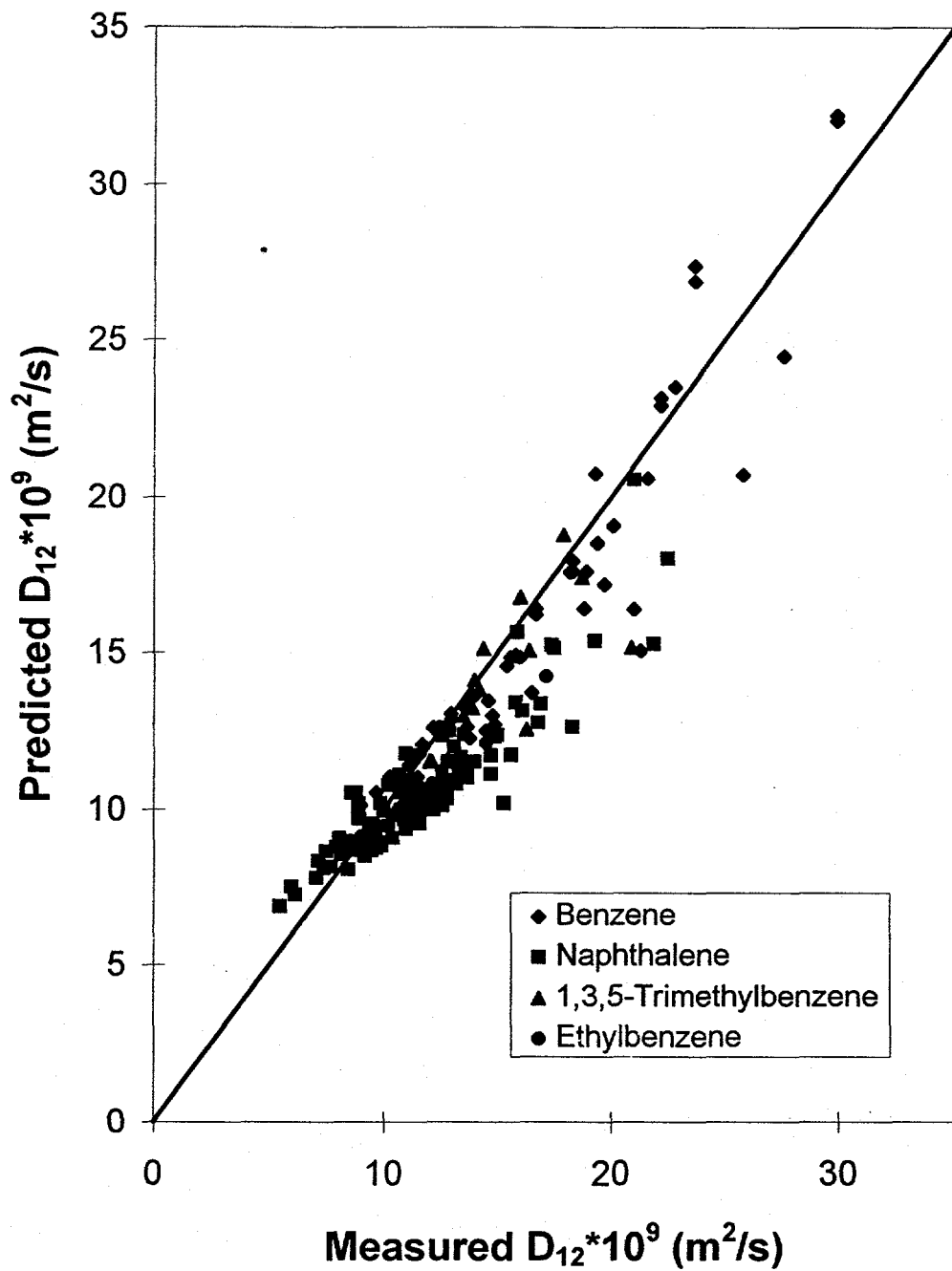


Figure 1. Comparison of experimental and predicted values of diffusion coefficients of aromatics in supercritical carbon dioxide.

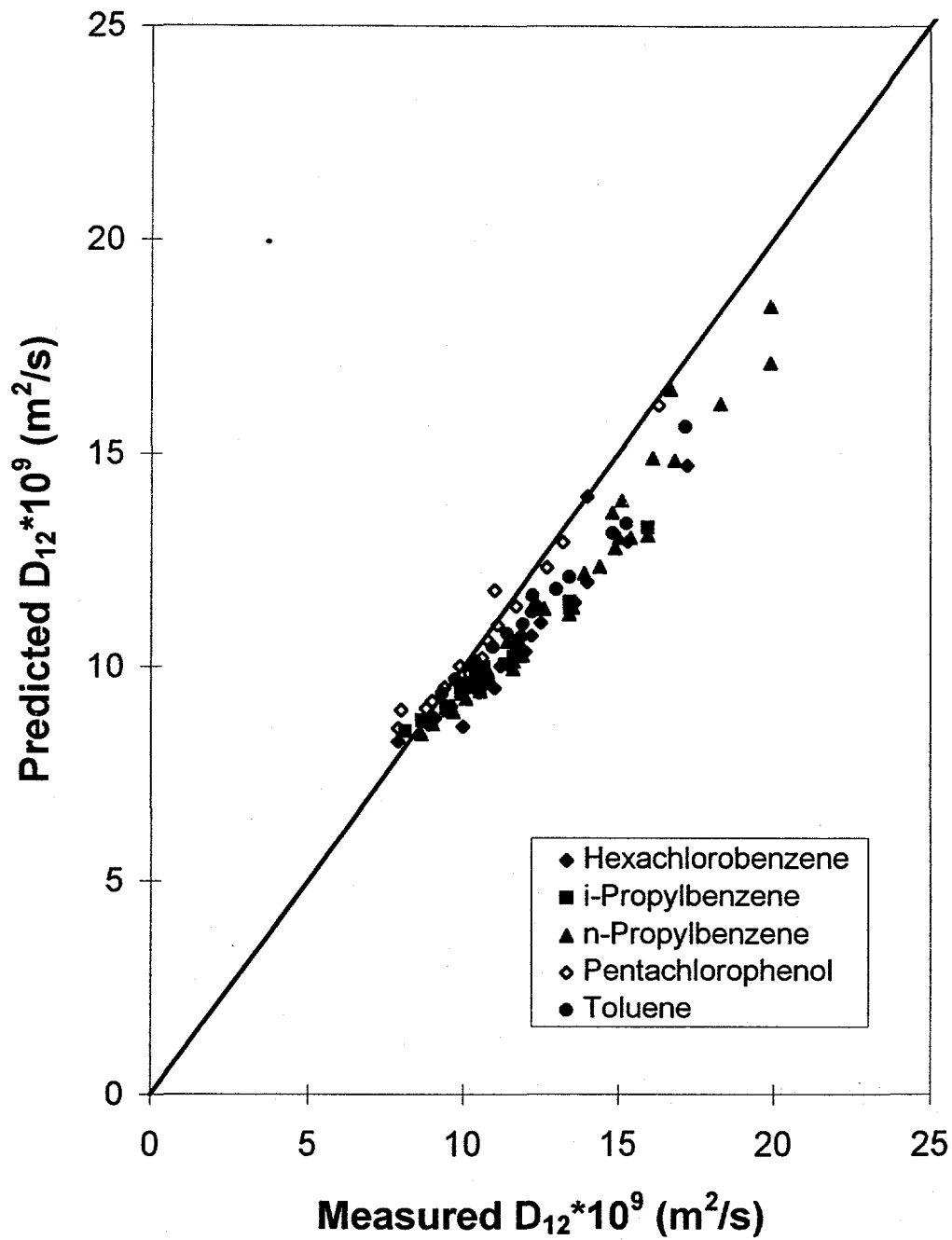


Figure 2. Comparison of experimental and predicted values of diffusion coefficients of branched aromatics in supercritical carbon dioxide.

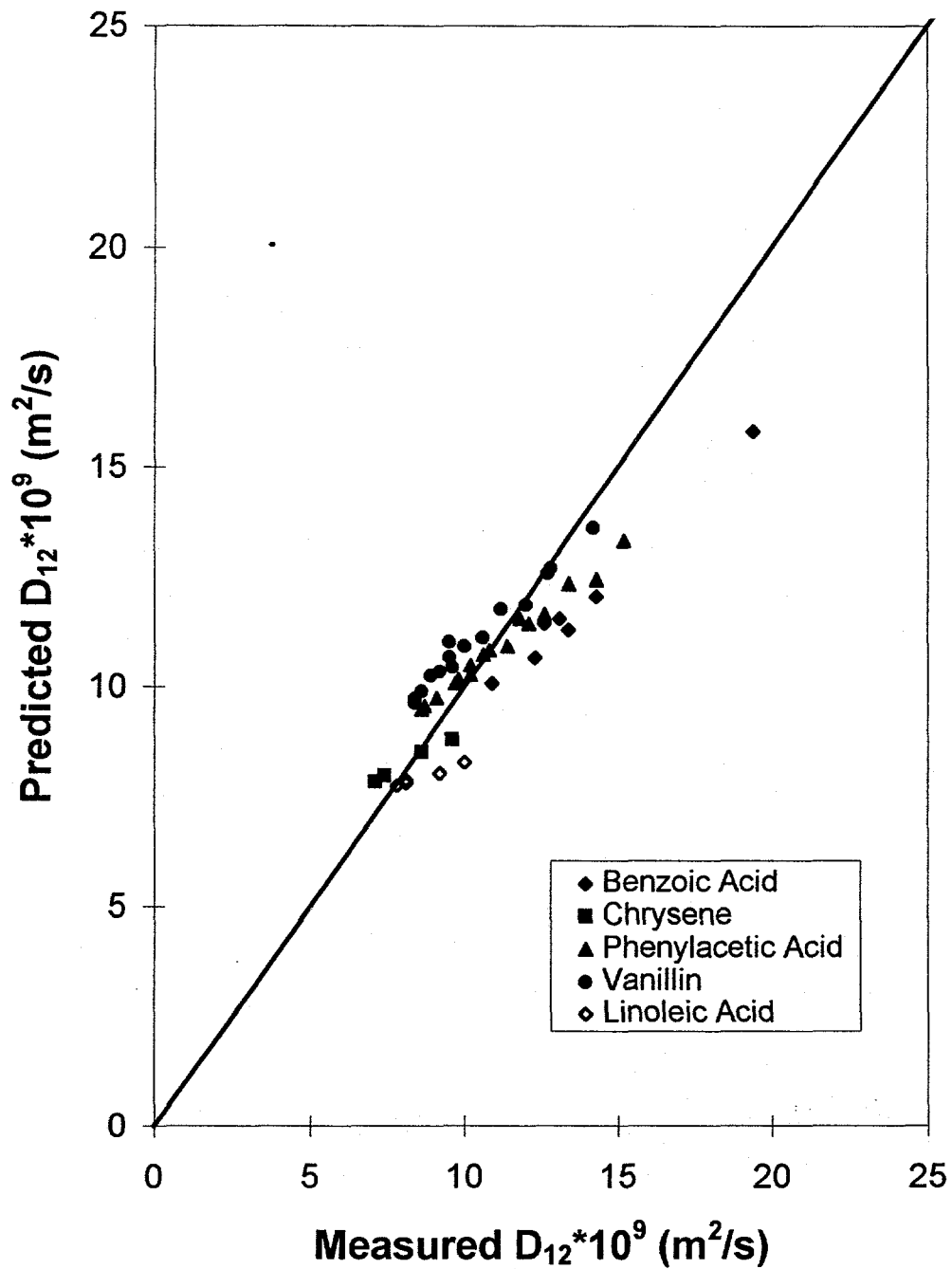


Figure 3. Comparison of experimental and predicted values of diffusion coefficients of various solutes in supercritical carbon dioxide.

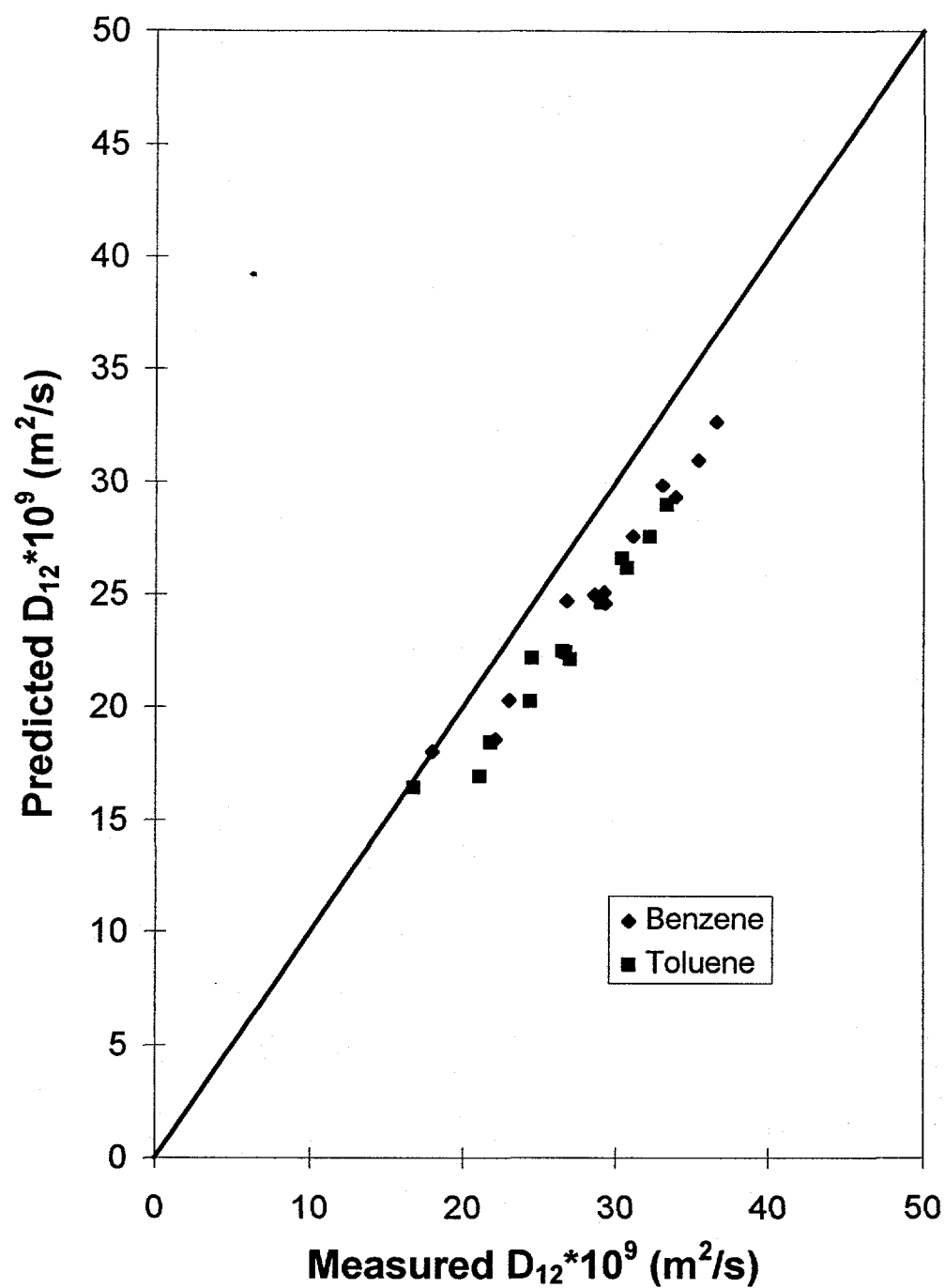


Figure 4. Comparison of experimental and predicted values of diffusion coefficients in supercritical ethanol.

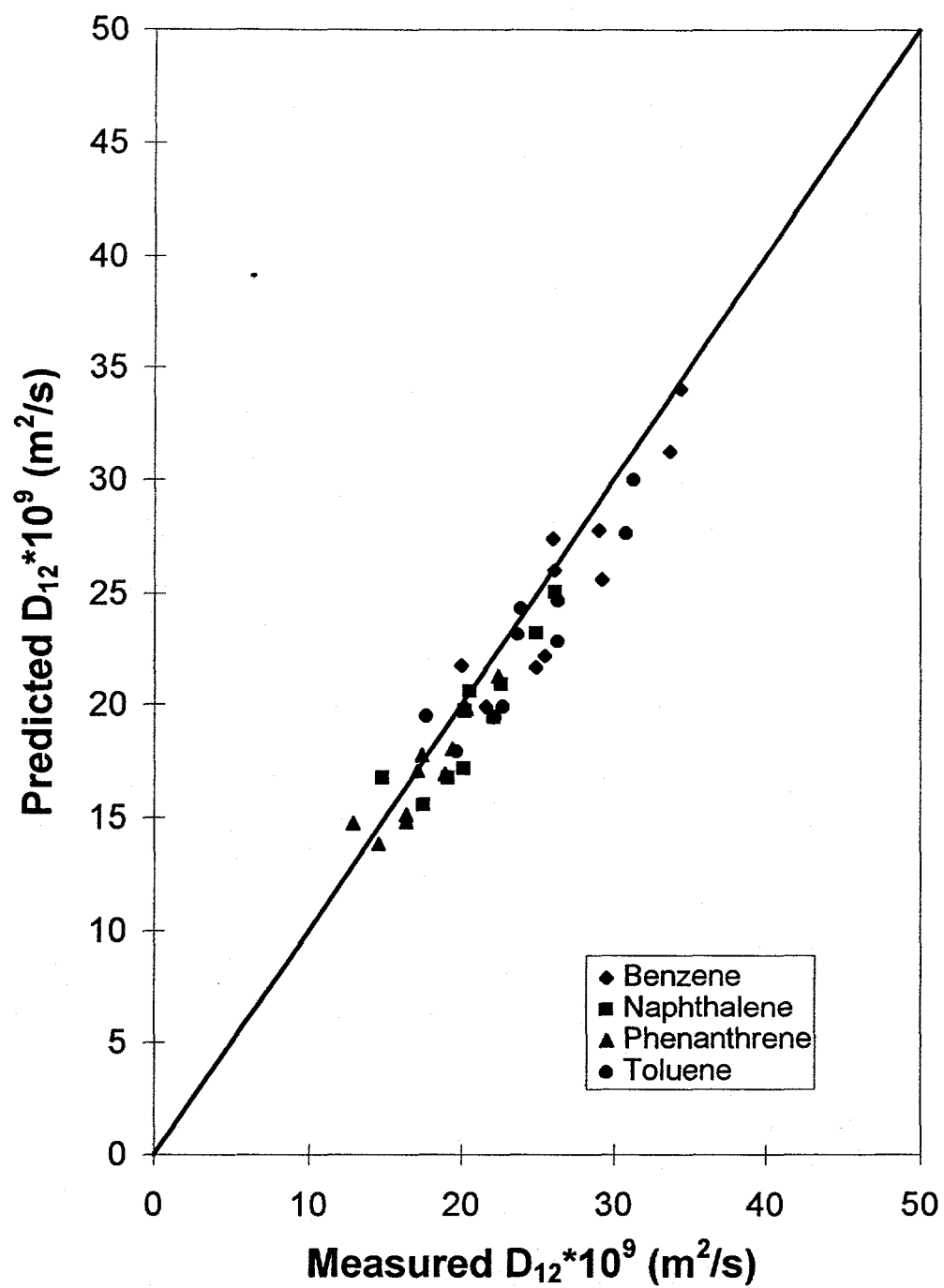


Figure 5. Comparison of experimental and predicted values of diffusion coefficients in supercritical 2-propanol.

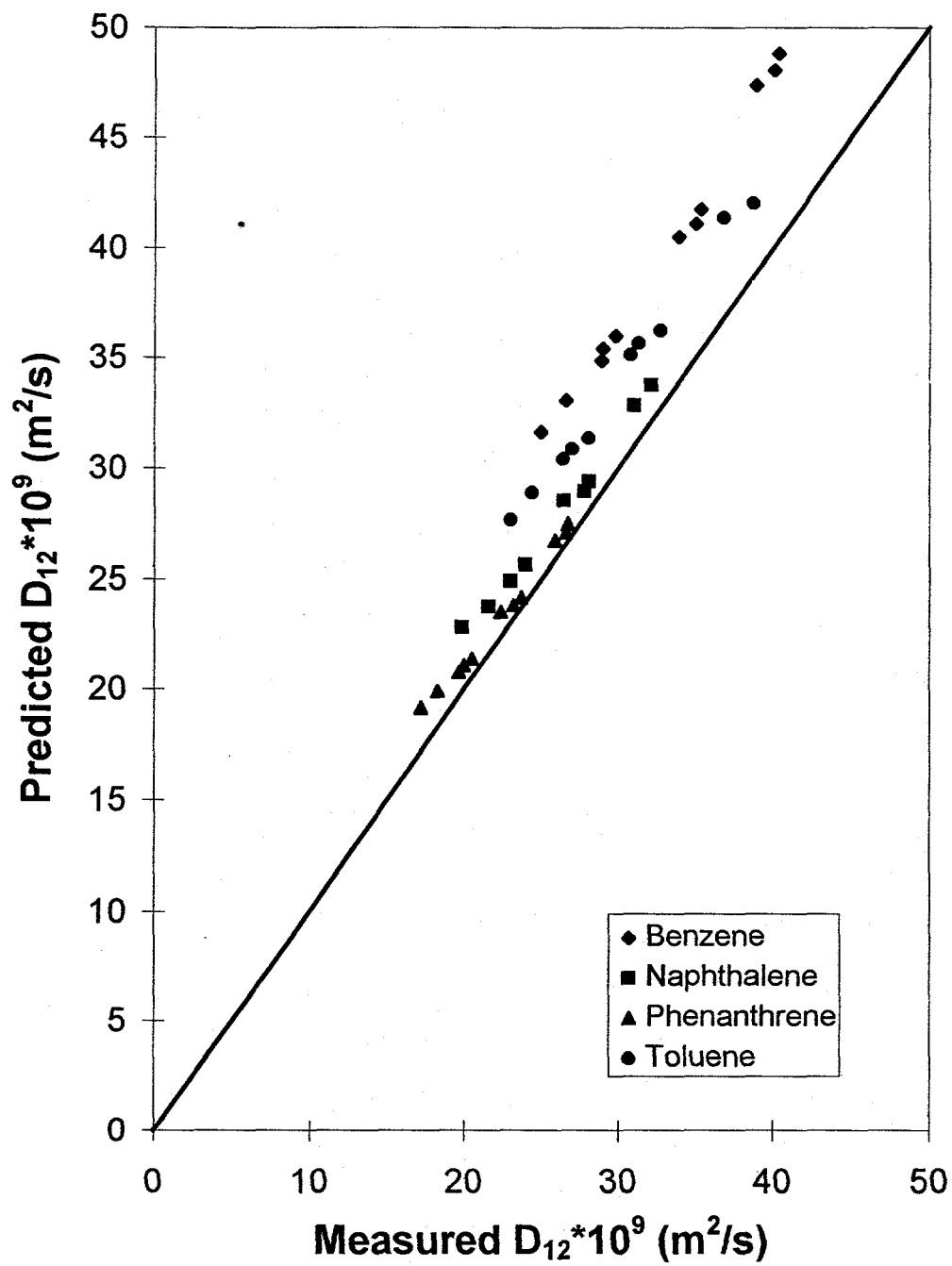


Figure 6. Comparison of experimental and predicted values of diffusion coefficients in supercritical 2,3-Dimethylbutane.

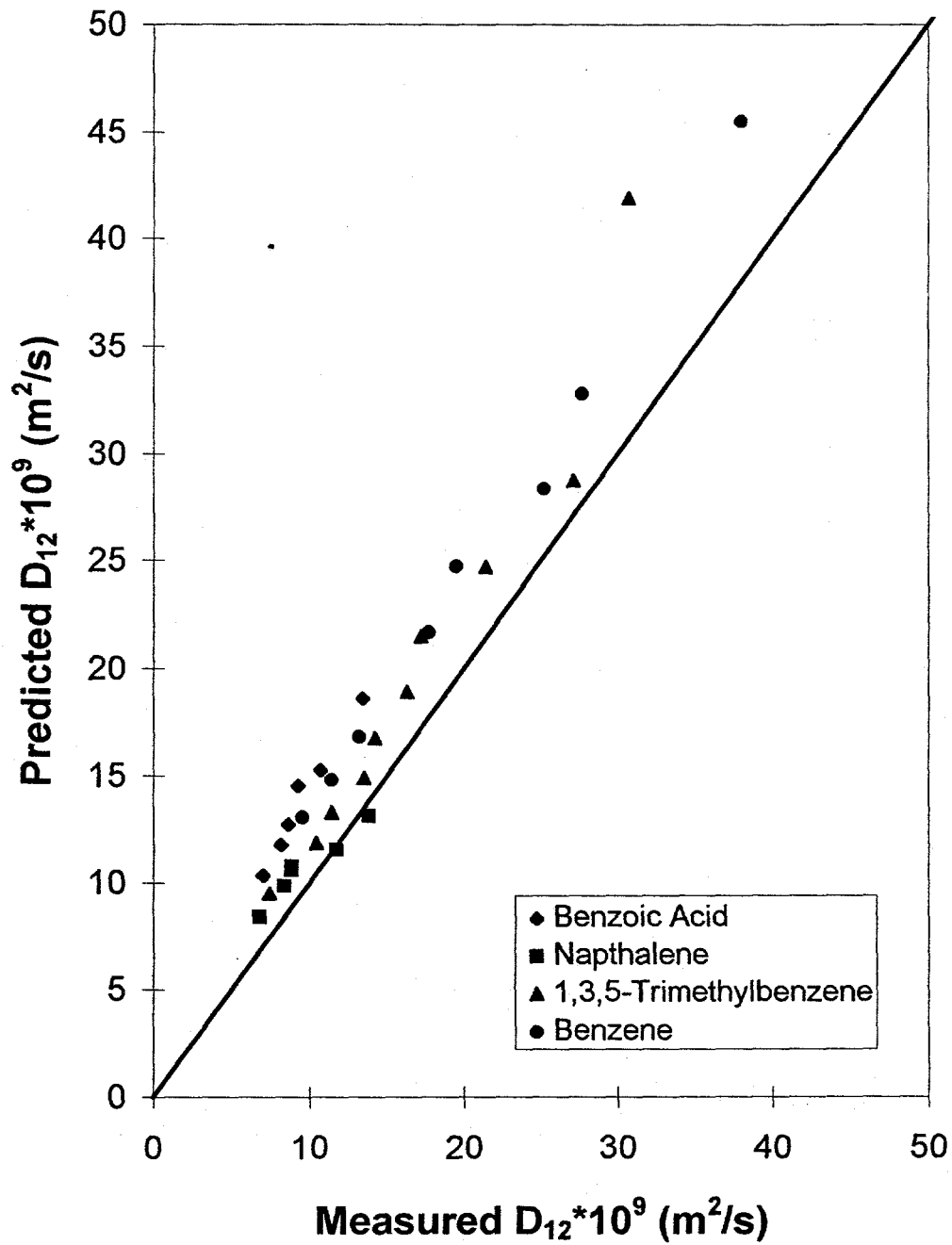


Figure 7. Comparison of experimental and predicted values of diffusion coefficients of acids and alkenes in supercritical sulphurhexafluoride.

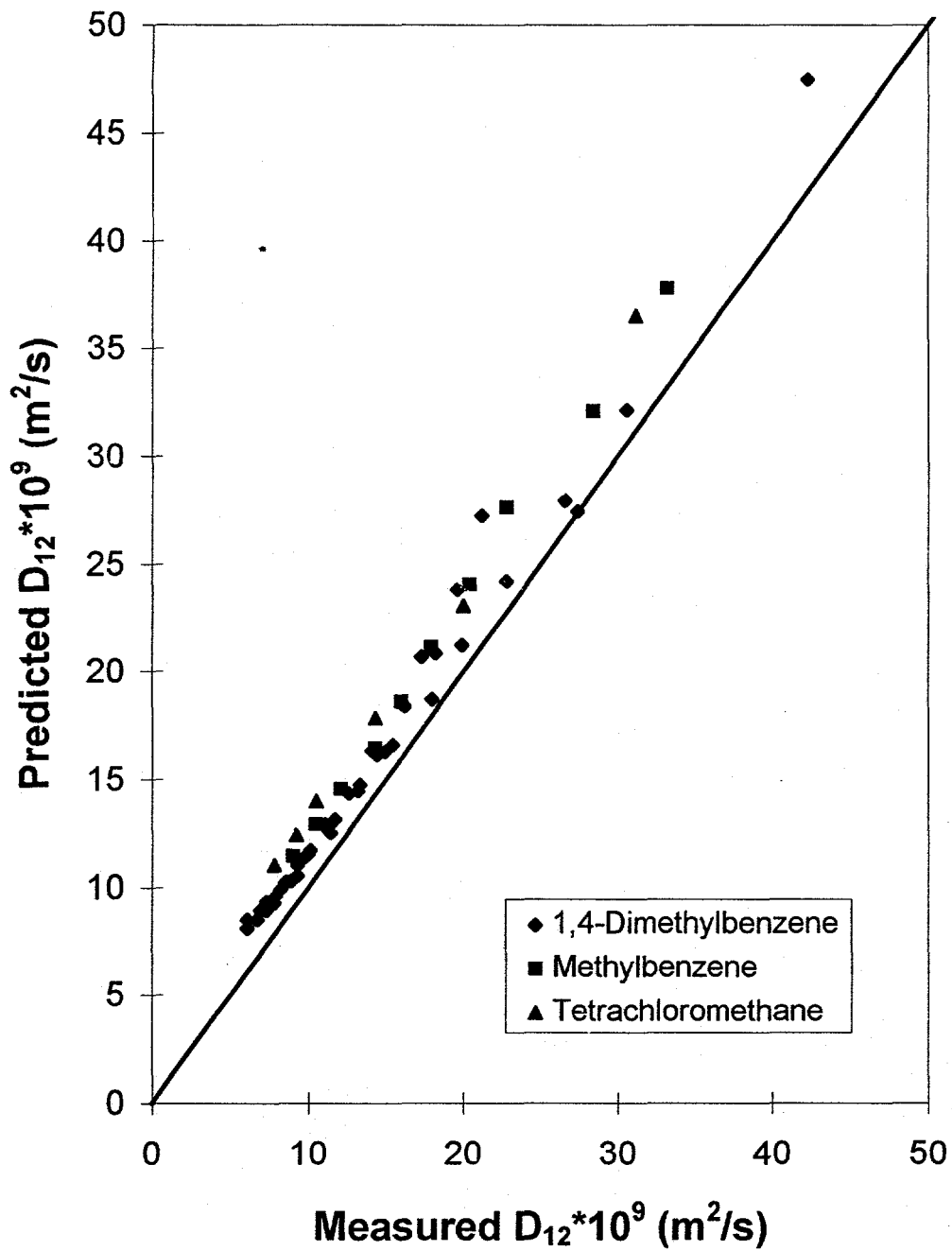


Figure 8. Comparison of experimental and predicted values of diffusion coefficients of various solutes in supercritical sulphurhexafluoride.

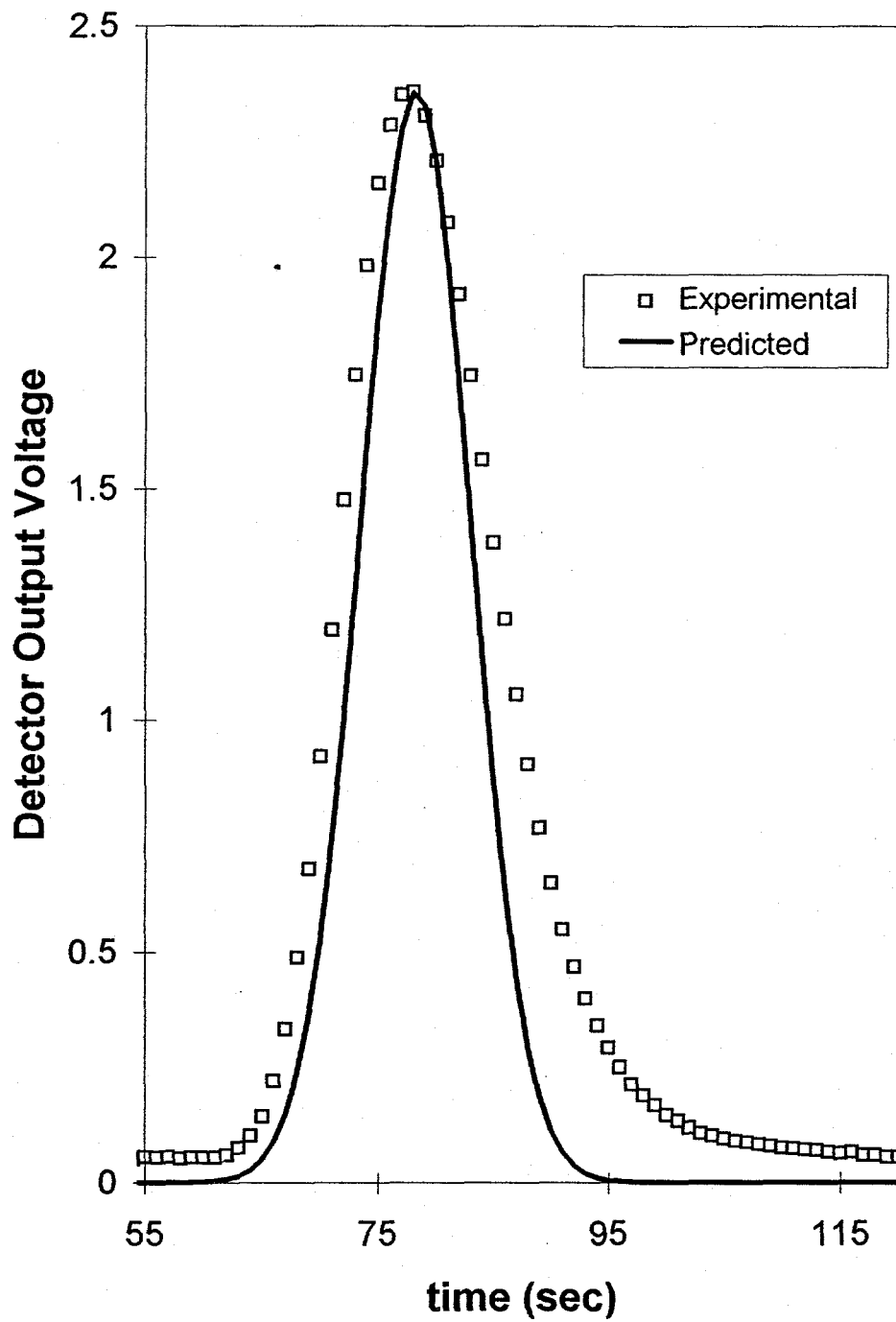


Figure 9. Comparison of measured voltage data to predicted value by Gaussian distribution for diffusion of 2-heptanone in supercritical carbon dioxide.

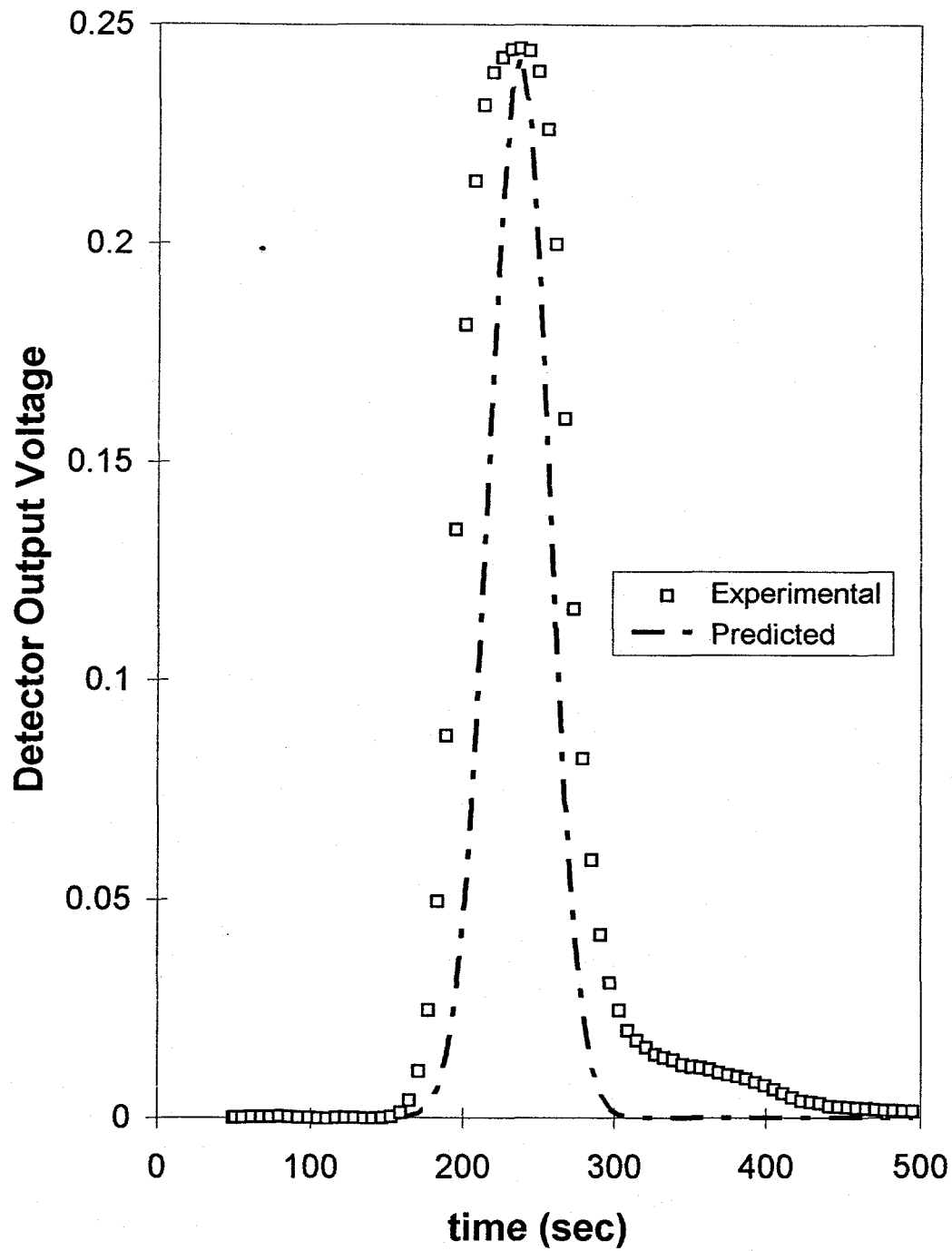


Figure 10. Comparison of measured voltage data to predicted value by Gaussian distribution for diffusion of butric acid ethyl ester in supercritical carbon dioxide.