

Diffusion Coefficients of Carbon Dioxide in Eight Hydrocarbon Liquids at Temperatures between (298.15 and 423.15) K at Pressures up to 69 MPa

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Abstract

We report experimental measurements of the mutual diffusion coefficients in binary systems comprising CO₂ + liquid hydrocarbon measured at temperatures between (298.15 and 423.15) K and at pressures up to 69 MPa. The hydrocarbons studied were the six normal alkanes hexane, heptane, octane, decane, dodecane and hexadecane, one branched alkane, 2,6,10,15,19,23-hexamethyltetracosane (squalane), and methylbenzene (toluene). The measurements were performed by the Taylor Dispersion method at effectively infinite dilution of CO₂ in the alkane, and the results have a typical standard relative uncertainty of 2.6 %. Pressure was found to have a major impact, reducing the diffusion coefficient at a given temperature by up to 55 % over the range of pressures investigated. A correlation based on the Stokes-Einstein model was investigated in which the effective hydrodynamic radius of CO₂ was approximated by a linear function of the reduced molar volume of the solvent. This represented the data for the normal alkanes only with an average absolute relative deviation (AAD) of 5 %. A new universal correlation, based on the rough-hard-sphere theory, was also developed which was able to correlate all the experimental data as a function of reduced molar volume with an AAD of 2.5 %.

1. Introduction

Diffusion coefficients of CO₂ in hydrocarbon liquids are important in a variety of industrial mass-transfer processes, in enhanced oil recovery (EOR) with injected CO₂, and also in CO₂ storage processes utilising depleted oil fields. In CO₂-EOR, supercritical CO₂ is injected to maintain reservoir pressure and to sweep oil towards production wells. Depending upon the type of oil and the reservoir conditions of temperature and pressure, the CO₂ may be either partially or fully miscible with the oil. In either case, dissolution of CO₂ in the oil has the effect of reducing the oil-phase viscosity, thereby helping to mobilise it. The rate of CO₂ dissolution is governed by a number of factors including thermophysical properties of the oil-CO₂ system, especially the phase behaviour and diffusion coefficients. A similar situation exists for CO₂ storage in reservoirs containing residual hydrocarbons, where significant amounts of CO₂ may be trapped by dissolution into the oil at a rate that is also influenced by the diffusion coefficients.

Unfortunately, there is presently no rigorous method for predicting the diffusion coefficient of gaseous or supercritical solutes such as CO₂ in hydrocarbons at elevated pressures, and the experimental data are also scarce.¹ Concerning mutual diffusion in dilute solution of CO₂ in n-alkane liquids, most of the available data pertain to pressures near to 0.1 MPa. Guzman and Garrido used an NMR technique to measure the diffusion coefficient of CO₂ in normal alkanes from hexane to heptadecane at $T = 298.15$ K.² Takeuchi et al.³ reported diffusion coefficients for CO₂ in hexane and heptane at $T = 298.15$ K and $p = 0.1$ MPa, while Luthjens et al.⁴ reported data for CO₂ diffusion in hexane at the same conditions. McManamey and Woollen⁵ provide data for CO₂ diffusion in tetradecane at $T = (298.5 \text{ and } 323.15)$ K and $p = 0.1$ MPa. Additional data have been reported for CO₂ diffusion in heptane at $T = 293$ K,⁶ dodecane at $T = (304 \text{ to } 566)$ K,⁷ and hexadecane at $T = (298 \text{ to } 564)$ K;^{2, 7, 8} these studies were restricted to pressures below 3.5 MPa and shed little light on the dependence of the diffusion coefficient upon pressure. Wang et al.^{9, 10} have studied CO₂ diffusion in octane and tetradecane under pressure of up to 4 MPa but these measurements were carried out at variable finite concentrations of CO₂ and do not provide information on the dependence of the diffusion coefficient on pressure at constant composition. Mutual diffusion coefficients for dilute solution of CO₂ in methylbenzene have been reported at $p = 0.1$ MPa over the temperature range (298 to 348) K.^{3, 5, 11} Some more complex systems have been studied; for example, Zhang et al.¹² measured the diffusion coefficient of CO₂ in a heavy crude oil at $T \approx 293$ K and $p = 2.8$ MPa. Summarising the literature, we note that the experimental data are few and that the dependence of the diffusion coefficient upon pressure has not been well studied for dilute solutions of CO₂ in hydrocarbon liquids. Accordingly, one objective of the current research was to address that deficiency through new experimental measurements of CO₂ diffusion in simple hydrocarbon liquids.

In this work we apply the well-established Taylor dispersion technique which has been used previously to determine the diffusion coefficient of gaseous solutes in both aqueous¹ and organic solvents.^{7, 11} This technique exploits the combined effects of axial dispersion, primarily due to a parabolic velocity profile, and radial dispersion, due to molecular diffusion, on a solute in laminar flow. These combined effects produce a Gaussian concentration distribution which when treated with the approach of Taylor¹³ and Aris¹⁴ yields the diffusion coefficient. The technique is relatively quick, is based upon a rigorous working equation, and allows measurements to be performed under extreme conditions of temperature and pressure.¹⁵ The present work extended over a range of temperatures from (298 to 423) K at which all of the

hydrocarbon solvents are well below their critical temperatures, the lowest of which (for hexane) is approximately 508 K.¹⁶

A second objective of the current work was to develop further simple models that can be used to predict diffusion coefficients of CO₂ in hydrocarbon liquids. Accordingly, the results of the present experimental study have been used to refine models based on the Stokes-Einstein equation and the rough hard sphere theory.

In the remainder of this article, we review the two theoretical approaches to be considered, detail the experimental approach, and finally analyse the experimental data in terms of the chosen models.

2. Theoretical Background

2.1 Stokes-Einstein Model

The Stokes-Einstein equation is a simple model that captures several key features of the diffusion of single dilute solutes. According to this equation, the mutual diffusion coefficient of the solute at infinite dilution is given by

$$D_{12} = k_B T / (n_{SE} \pi a \eta), \quad (1)$$

where k_B is Boltzmann's constant, T is temperature, n_{SE} is the Stokes-Einstein number, η is the solvent viscosity, and a is the hydrodynamic radius of the solute. This model was developed for the diffusion of macroscopic spherical particles in a continuum and, with a no-slip boundary condition, the Stokes-Einstein number is rigorously equal to 6. When applied to molecules, n_{SE} is often set equal to 4, which is the theoretical results for a spherical particle with a slip boundary condition.¹⁷ As with the Stokes-Einstein number, the radius a is precisely defined for macroscopic spheres but the subject to some ambiguity when the model is applied to molecular diffusion. Nevertheless, the Stokes-Einstein equation generally captures correctly the dependence of solute diffusion coefficients on temperature and solvent viscosity. The model can be successful in describing diffusion in dilute solutions when either the hydrodynamic radius is treated as a weakly-temperature-dependent parameter¹ or the viscosity is raised to an empirical power.¹⁸

2.2 Rough-Hard-Sphere Theory

Given the somewhat over-simplified nature of the Stokes-Einstein model, an alternative modelling approach based on the kinetic theory of rough hard spheres may be preferred. The rough-hard-sphere theory has been successfully used in various forms to correlate transport properties of both pure¹⁹⁻²⁶ and binary systems.^{21, 27-31} For mutual diffusion, the theory may be built up starting from the kinetic-theory expression for the mutual diffusion coefficient of a dilute binary mixture of smooth hard spherical molecules:

$$[nD_{12}]_0 = \frac{3}{8\sigma_{12}^2} \sqrt{\frac{k_B T}{2\pi\mu_{12}}}. \quad (2)$$

Here, n is the number density, σ_{12} is the arithmetic mean of the diameters σ_1 of the solute and σ_2 of the solvent molecules, and μ_{12} is the reduced mass.³² An expression for the mutual diffusion coefficient in a dense mixture of smooth hard spheres was given by Enskog et al.³³ in 1939, who considered the increase in the molecular collision frequency arising from the

volume excluded by the molecular cores and concluded that the dilute-gas result should be divided by the value of the unlike radial distribution function at contact, $g_{12}(\sigma_{12})$.^{27, 34, 35} This term is given at infinite dilution with sufficient accuracy by

$$g_{12}(\sigma_{12}) = \frac{1}{1-\xi} + \frac{3\xi}{(1+\sigma_2/\sigma_1)(1-\xi)^2} + \frac{\xi^2}{(2\sigma_2/\sigma_1)(1-\xi)^3}, \quad (3)$$

where $\xi = \pi n \sigma_2^2 / 6$ is the solvent packing density.^{36, 37} Correlated molecular collisions, which are neglected in the Enskog theory, play an increasingly important role as the density increases. This effect may be evaluated from molecular-dynamics (MD) simulations of hard-sphere mixtures and accounted for by an additional factor C_{12} such that the diffusion coefficient for smooth hard spheres at any density is given by:^{28, 38}

$$[nD_{12}]_{\text{SHS}} = \left(\frac{C_{12}}{g_{12}(\sigma_{12})} \right) [nD_{12}]_0. \quad (4)$$

Unlike their smooth counterparts, rough hard spheres can exchange translational and rotational energy in collisions. It has been shown that the effect of this exchange is to modify the expression for the mutual diffusion by a translational-rotational coupling factor A_{12} that is independent of temperature and density,³⁴ such that the final expression for the mutual diffusion coefficient at infinite dilution in a dense binary mixture of rough hard spheres is

$$[nD_{12}]_{\text{RHS}} = \left(\frac{A_{12}C_{12}}{g_{12}(\sigma_{12})} \right) [nD_{12}]_0. \quad (5)$$

Since hard-sphere systems are athermal, $A_{12}C_{12}/g_{12}(\sigma_{12})$ will generally depend upon the density and composition of the mixture but not on temperature.

In developing the theory further, it is useful to define a dimensionless reduced diffusion coefficient as follows:

$$D_{12}^* = \frac{[nD_{12}]}{[nD_{12}]_0} \left(\frac{V}{V_{0,12}} \right)^{2/3} \left(\frac{V_{0,12}}{V_{0,2}} \right)^{2/3}. \quad (6)$$

Here, $[nD_{12}]_0$ is the product of the number density and the mutual diffusion coefficient in the limit of infinite dilution, V is the molar volume, and $V_{0,2}$ and $V_{0,12}$ are molar core volumes based on the following definitions:

$$V_{0,1} = \frac{N_a \sigma_1^3}{\sqrt{2}}, \quad (7)$$

$$V_{0,2} = \frac{N_a \sigma_2^3}{\sqrt{2}}, \quad (8)$$

and

$$V_{0,12} = \frac{N_a \sigma_{12}^3}{\sqrt{2}} = (V_{0,1}^{1/3} + V_{0,2}^{1/3})^3 / 8, \quad (9)$$

where N_a is Avogadro's constant. With this definition and eq (2) for $[nD_{12}]_0$, the reduced mutual diffusion coefficient is given by

$$D_{12}^* = \left(\frac{8\pi^{1/2} 2^{1/3} N_a^{1/3}}{3A_{12}} \right) \left(\frac{2M_{12}}{RT} \right)^{1/2} \left(\frac{V_{0,12}}{V_{0,2}} \right)^{2/3} \left(\frac{D_{12}}{V^{1/3}} \right), \quad (10)$$

where $M_{12} = M_1 M_2 / (M_1 + M_2)$ is the reduced molar mass and M_i is the molar mass of pure component i . We note that eq (10) reduces to the dimensionless self-diffusion coefficient defined by Assael et al.¹⁹ in the case where the solute and solvent molecules are identical. Following the approach used for the transport properties of pure fluids, these results for rough hard spherical molecules are applied to real non-spherical molecules, first, by allowing the molar core volumes to be weak functions of temperature and second by treating A_{12} as an empirical ‘roughness factor’ to be determined for each solute-solvent pair.

According to eqs (5) and (6), the reduced diffusion coefficient in the hard sphere system is given by

$$D_{12}^* = \left(\frac{C_{12}}{g_{12}(\sigma_{12})} \right) \left(\frac{V}{V_{0,2}} \right)^{2/3}, \quad (11)$$

where C_{12} is generally a function of three macroscopic ratios: $V/V_{0,2}$, $V_{0,2}/V_{0,1}$ and M_2/M_1 . In the case of self diffusion, the latter two are unity and the reduced diffusion coefficient is then rigorously a function of the reduced molar volume of the solvent only, e.g. for the pure solvent:

$$D_{22}^* = F_{22}(V/V_{0,2}). \quad (12)$$

The universal function F_{22} can in principle be obtained from the MD results but has in practise been established from experimental data.¹⁹ For binary hard-sphere mixtures at infinite dilution of the solute 1, Eastal and Woolf³⁸ report MD results for C_{12} calculated on a regular grid in the following ranges: $1.5 \leq V/V_{0,2} \leq 2.0$, $1.0 \leq \sigma_2/\sigma_1 \leq 2.0$, and $0.6 \leq M_2/M_1 \leq 10$. Combining these results with $g_{12}(\sigma_{12})$ from eq (3) yields D_{12}^* and also D_{22}^* in the binary hard-sphere system with estimated relative uncertainties of (1 to 2) %. These data show that D_{12}^* and D_{22}^* are linear functions of reduced volume over the range investigated; additionally, D_{12}^* increases with increasing size ratio σ_2/σ_1 and decreases with increasing mass ratio M_2/M_1 . This suggests that a universal correlation similar to eq (12) might not be possible for the case of binary systems. However, an important point to note when applying the model to real systems is that molecular size and mass are not independent quantities. In fact, for the normal alkanes investigated in this work, Figure 1 shows that the molar core volume is a simple linear function of the molar mass. In this figure, the molar core volumes were evaluated at $T = 298.15$ K based on literature correlations derived from the analysis of pure-component transport properties.^{20, 39, 40}

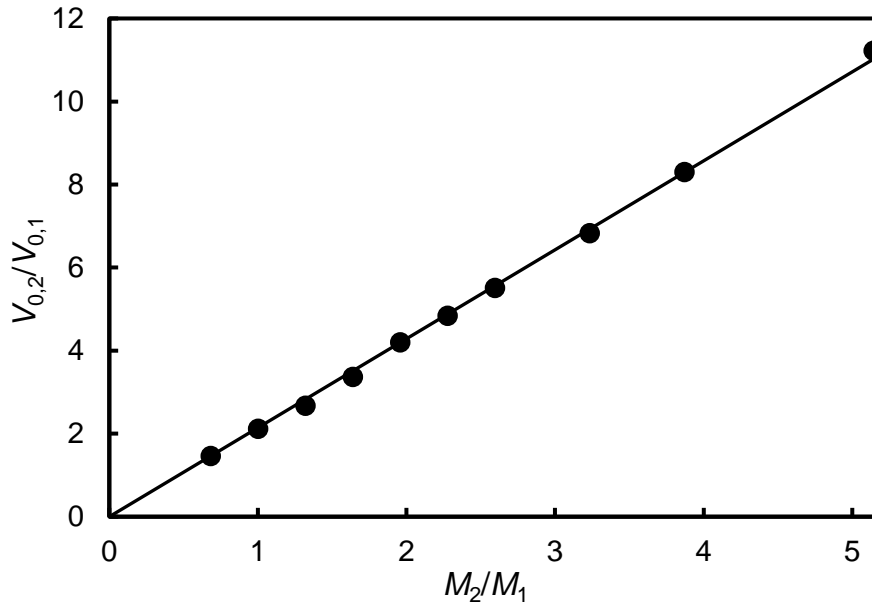


Figure 1. Ratio $V_{0,2}/V_{0,1}$ of the molar core volumes as a function of the ratio M_2/M_1 of molar masses, where component 1 is CO_2 and component 2 belongs to the series of n -alkane with carbon numbers 2 to 8 inclusive, 10, 12 and 16.

For any group of solvents in which $V_{0,2}$ is a unique function of M_2 , D_{12}^* obviously reduces to a function of just two variables, e.g. $V/V_{0,2}$ and M_2/M_1 . Remarkably, when interpolated to a path of constant $M_1 V_{0,2}/(M_2 V_{0,1})$, the MD results for D_{12}^* actually collapse to a set of closely-spaced parallel lines which, in view of the relative uncertainty of the MD data, constitute an essentially unique function of $V/V_{0,2}$ alone. This is illustrated in Figure 2 for the cases in which $M_1 V_{0,2}/(M_2 V_{0,1})$ is 0.86 and 2.1, representative of CH_4 and CO_2 diffusion in normal alkanes respectively. The data plotted here relate to the grid of $V/V_{0,2}$ and σ_2/σ_1 investigated by Eastale and Woolf together with the interpolation formula with respect to M_2/M_1 that they specified.³⁸ Other values of $M_1 V_{0,2}/(M_2 V_{0,1})$ also lead to a linear dependence of D_{12}^* on $V/V_{0,2}$ but with different parameters. The reduced self diffusion coefficient of the pure solvent, D_{22}^* , is also plotted in Figure 2 and follows yet another linear relationship in the region of reduced volume considered. From this analysis, we can conclude that, for a given solute and a series of solvents in which $M_1 V_{0,2}/(M_2 V_{0,1})$ is sensibly constant, the reduced diffusion coefficient D_{12}^* should be an essentially-unique function of the reduced molar volume $V/V_{0,2}$, generally different from the case of self-diffusion:

$$D_{12}^* = F_{12}(V/V_{0,2}). \quad (13)$$

The MD results suggest that F_{12} is a linear function for $1.5 \leq V/V_{0,2} \leq 2.0$ but this might not be the case outside that range.

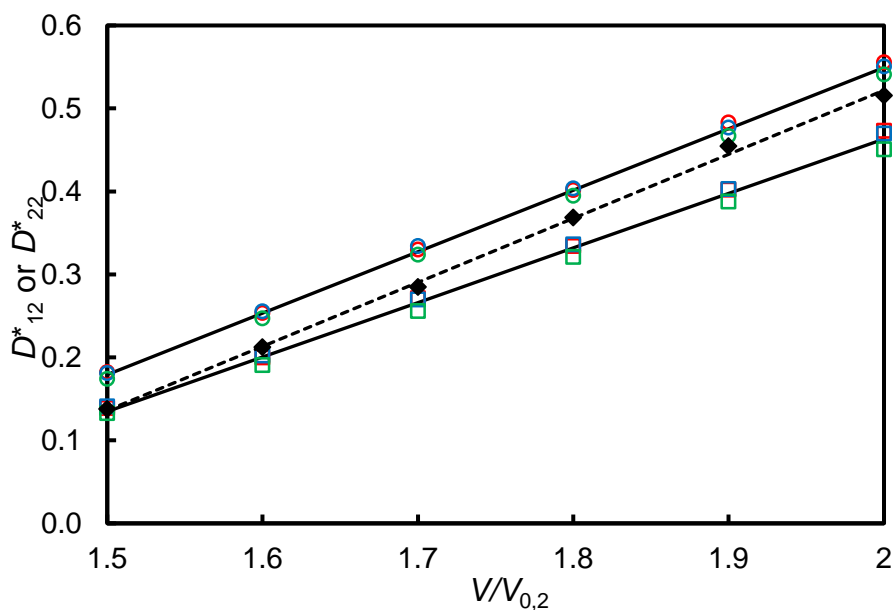


Figure 2. Reduced mutual diffusion coefficient D_{12}^* for hard-sphere solutes 1 at infinite dilution in hard-sphere solvents 2 as a function of reduced molar volume $V/V_{0,2}$ for different size ratios σ_2/σ_1 . MD simulation data at $\sigma_2/\sigma_1 = 1.6$ (red), 1.8 (blue) and 2.0 (green): \circ , $M_1 V_{0,2}/(M_2 V_{0,1}) = 2.1$; \square , $M_1 V_{0,2}/(M_2 V_{0,1}) = 0.86$; \blacklozenge , reduced self diffusion coefficient D_{22}^* for the pure hard-sphere solvent. Lines are linear regressions.

Somewhat similar conclusions were deduced by Matthews *et al.*²² and Rodden *et al.*⁴¹ on the basis of combinations of MD and experimental data showing that D_{12}/\sqrt{T} behaves as a linear function of molar volume. Matthews *et al.* proposed simple correlations based on such a linear equation in which the only parameters required are the molar mass of the solute and the critical molar volume of the solvent.²⁸

3. Experimental Section

3.1 Methodology

Fig. 3 is a schematic diagram of the Taylor dispersion apparatus used in this work; a full description of this equipment can be found in Cadogan *et al.*¹ One modification was implemented in the present study, which was to heat the syringe pump and the portions of the flow path outside the thermostatic bath to a temperature of approximately 313 K so as to avoid freezing of hexadecane at high pressures.

The chemicals used are detailed in Table 1. The solvents were degassed before filling the pump using an in-line vacuum degasser. The procedures for acquiring and analysing the raw data were as described previously.¹ Solutions of CO_2 in the hydrocarbon under study were prepared at a pressure no greater than 0.5 MPa. Once thermal equilibrium was established in the thermostatic bath and steady-state flow was established, as evidence by a constant pressure upstream of the column, a series of solution injections was made. Typically, 4 to 6 repeat measurements were made at each temperature and pressure from which the mean and relative standard deviation of the diffusion coefficients were calculated. The standard uncertainty of the temperature was $u(T) = 0.01$ K. In the case of pressure, the relative standard uncertainty of a single measurement was 0.25 % but pressures were typically found to drift

during the course of the repeated measurements at each nominal state point and, to account for this, we estimate the overall standard uncertainty of the pressure to be 0.5 MPa.

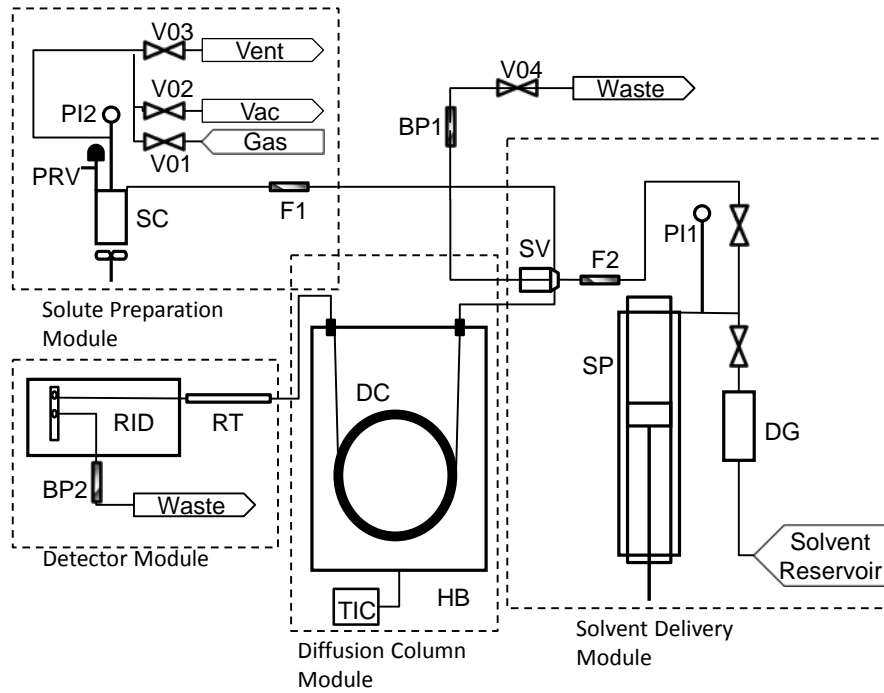


Figure 3. Schematic of the Taylor dispersion apparatus: DG, vacuum degasser; SP, syringe pump; P11 and P12, pressure transducers; F1 and F2, filters; SV, sample valve; DC, diffusion column; HB, thermostatic oil bath; TIC, temperature controller; RT, restriction tube; RID, refractive index detector; BP1 and BP2, back pressure valves; SC, saturation chamber; PRV; proportional relief valve; V01, V02 and V03, gas and vacuum valves; V04; solution outlet valve.¹

4. Experimental Results

The values of the diffusion coefficients for CO₂ in the respective hydrocarbons over the temperature range (298 to 423) K and pressures < 69 MPa are given in Tables 2 to 9. The overall standard relative uncertainty of the measured diffusion coefficients was calculated from the relation

$$u_r^2(D_{12}) = u_r^2(K) + 4u_r^2(R) + u_r^2(v) + [(\partial \ln D_{12} / \partial p)_T u(p)]^2 + [(\partial \ln D_{12} / \partial T)_p u(T)]^2, \quad (14)$$

where $u_r(X)$ denotes standard relative uncertainty and $u(X)$ standard uncertainty of variable X . In eq (14), K is the dispersion coefficient, R is the radius of the diffusion tube and v is the axial velocity of the solvent averaged over the cross section of the tube. The standard relative uncertainties appearing on the right of eq (15) were $u_r(K) = 2.0\%$, estimated from the repeatability of the dispersion measurements, $u_r(R) = 0.2\%$ and $u_r(v) = 0.5\%$, while the standard uncertainties of pressure and temperature are 0.5 MPa and 0.01 K, respectively. This led to $u_r(D) = 2.6\%$ for the systems investigated.

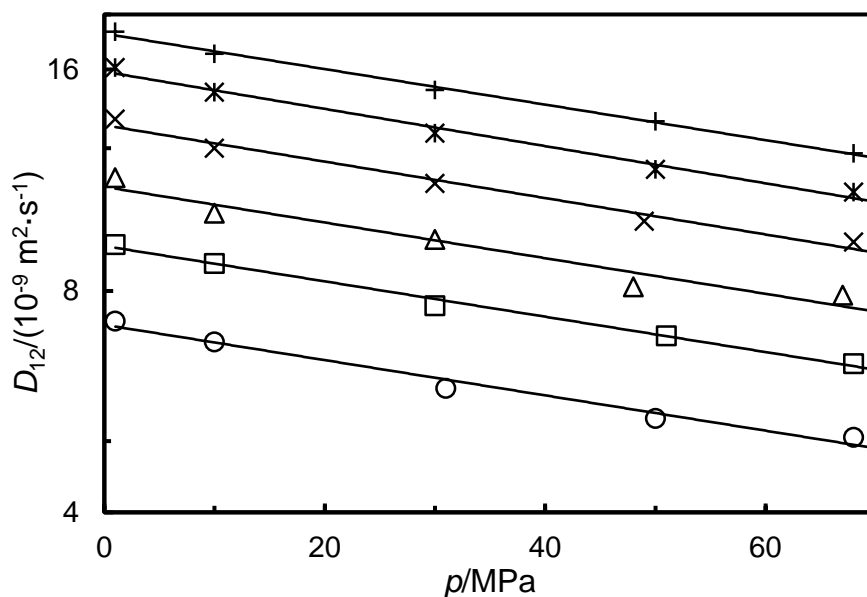


Figure 4. Diffusion coefficient D_{12} of CO₂ in heptane as a function of pressure p . This work: O, $T = 298$ K; □, $T = 323$ K; △, $T = 348$ K; ×, $T = 373$ K; *, $T = 398$ K; +, $T = 423$ K. Lines are regressions with eq (15). Note the logarithmic scale used on the vertical axis.

As expected, the diffusion coefficient increases with increasing temperature and declines with increasing pressure. Figure 4 shows the diffusion coefficient of CO₂ in heptane as a function of pressure along isotherms. In this case, D_{12} decreases by approximately 32 % between (1 and 69) MPa at a given temperature.

As discussed in the introduction, most of the data reported in the literature pertain to a pressure of 0.1 MPa. To facilitate a comparison with the literature at that pressure, the present results along each isotherm were fitted by the following empirical equation

$$D_{12} = D_0 \exp[-b(p - p_0)], \quad (15)$$

to determine the diffusion coefficient D_0 at $p = p_0 = 0.1$ MPa. At temperatures above the normal boiling temperature of the solvent, the D_0 relates to a hypothetical liquid state. Figure 4 shows that this provides a good representation of the data for heptane and the same was found to be true for each of the other systems. The coefficients D_0 and b determined in these fits, together with the standard deviation $\sigma(D_{12})$, are given in Table 10. Figure 5 compares the values of D_0 at $T = 298$ K with data from the literature for CO₂ diffusion in the normal alkanes. The agreement is generally very good, especially with the NMR data of Guzman and Cheng where the agreement is generally within the experimental uncertainty.² One exception is the datum of Luthjens et al.⁴ for hexane, which is some 17 % smaller than the present result.

Except in the case of squalane, the coefficient b , which expresses the pressure-dependence of D_{12} , was found to vary between (0.005 and 0.008) MPa⁻¹ in all our isothermal fits. However, this variation reflects mainly scatter in the data and the quality of the fit was almost the same when b was constrained to a constant value, independent of both the solvent and the temperature. The optimal value in that case is $b = 0.0062$ MPa⁻¹ corresponding to an average relative reduction in the value of D_{12} of 35 % between $p = 0.1$ MPa and $p = 69$ MPa. In the case of squalane, the value of b determined in our isothermal regressions increases at low

temperatures, reaching 0.0114 MPa^{-1} at $T = 298 \text{ K}$ and, at this temperature, D_{12} declines by some 55 % between $p = 0.1 \text{ MPa}$ and $p = 69 \text{ MPa}$.

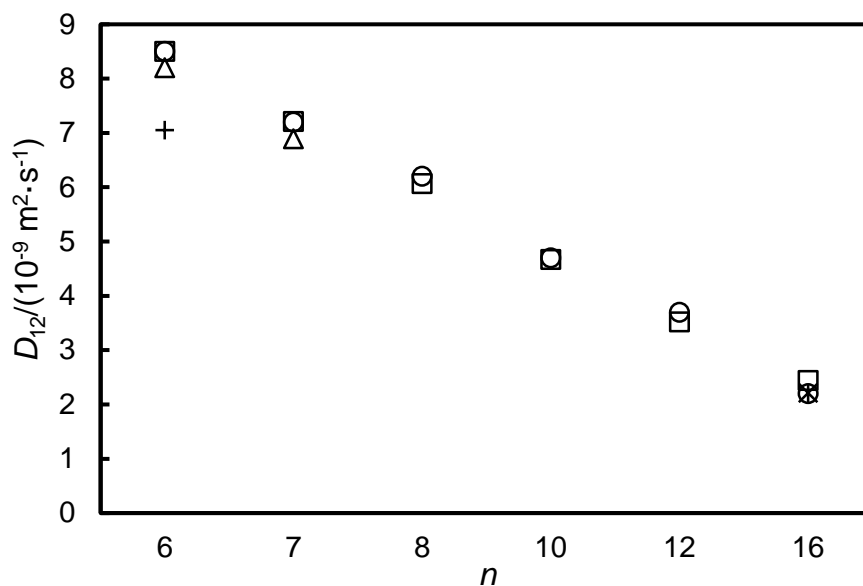


Figure 5. Diffusion coefficients D_{12} of CO_2 in normal alkanes at $T = 298.15 \text{ K}$ and $p = 0.1 \text{ MPa}$ as a function of the solvent carbon number n : O, this work (isothermal fit with equation 15); \square , Guzman and Garrido;² \triangle , Takeuchi et al.;³ +, Luthjens et al.;⁴ *, Hayduk and Cheng.⁸

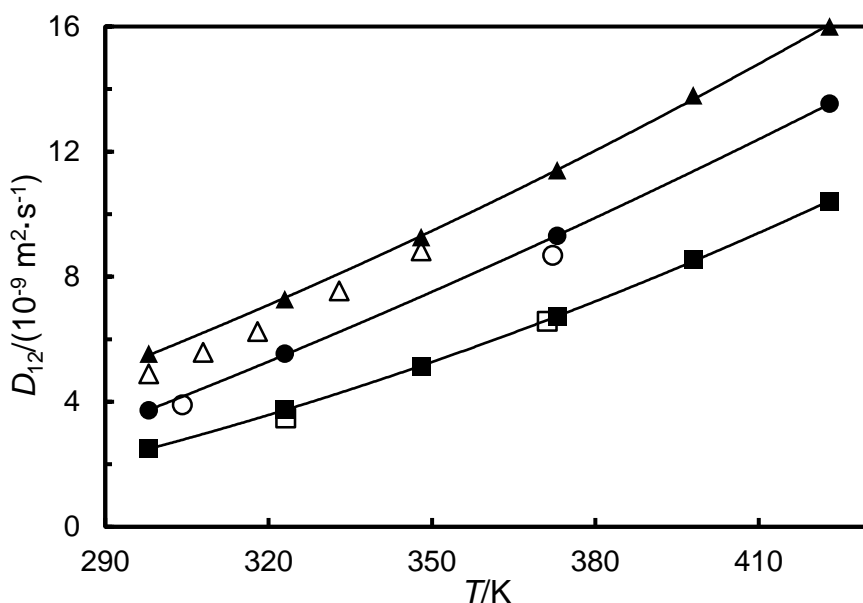


Figure 6. Diffusion coefficients D_{12} of CO_2 in three hydrocarbon liquids at infinite dilution and pressures below 1.5 MPa. This work: \blacktriangle , methylbenzene; \bullet , dodecane; \blacksquare , hexadecane. Literature: \triangle , methylbenzene;¹¹ O, dodecane;⁷ \square , hexadecane.⁷ Curves are quadratic function of temperature fitted to the present results.

The present results are compared with the available literature data at other temperatures in Figure 6. Here, the pressures vary between (0.1 and 1.5) MPa and, based on our findings, this variation is not significant. The present results for dodecane and hexadecane agree with those of Matthews *et al.*⁷ to within about 5 %, whereas the values reported by Snijder *et al.*¹¹ are about 10 % smaller than ours. The differences observed with the data of Matthew *et al.*,⁷

who state a repeatability of 5 %, are within the combined uncertainties. In the case of methylbenzene, the differences observed with the data of Snijder *et al.*,¹¹ who stated a repeatability of about 1 %, are larger than the combined uncertainty. Both sets of authors used the Taylor dispersion method.

4. Stokes-Einstein Model

The diffusion coefficient of CO₂ in all the investigated solvents was dependent on the system pressure. This can be rationalised by the increase in the solvent viscosity with pressure. The effect of pressure on these systems was contrary to the behaviour reported elsewhere for CH₄ diffusion in liquid hydrocarbons.⁴²

For purposes of analysis with eq (1), viscosities η and densities ρ for the solvents from n-hexane to n-dodecane were calculated using the NIST REFPROP software,⁴³ while for hexadecane and squalane recent correlations were employed.^{39, 40} The hydrodynamic radius corresponding to each measured diffusion coefficient was calculated using eq (1) and was found to be dependent on temperature, pressure and the solvent. For the normal alkanes, the hydrodynamic radius was found to correlate most strongly with the reduced density of the solvent. This is illustrated in Figure 7, where a is plotted as a function of ρ/ρ_c , where ρ_c is the critical density of the solvent. A linear expression relating the hydrodynamic radius to the reduced solvent density was therefore fitted as follows:

$$a/\text{nm} = 0.489 - 0.127(\rho/\rho_c). \quad (16)$$

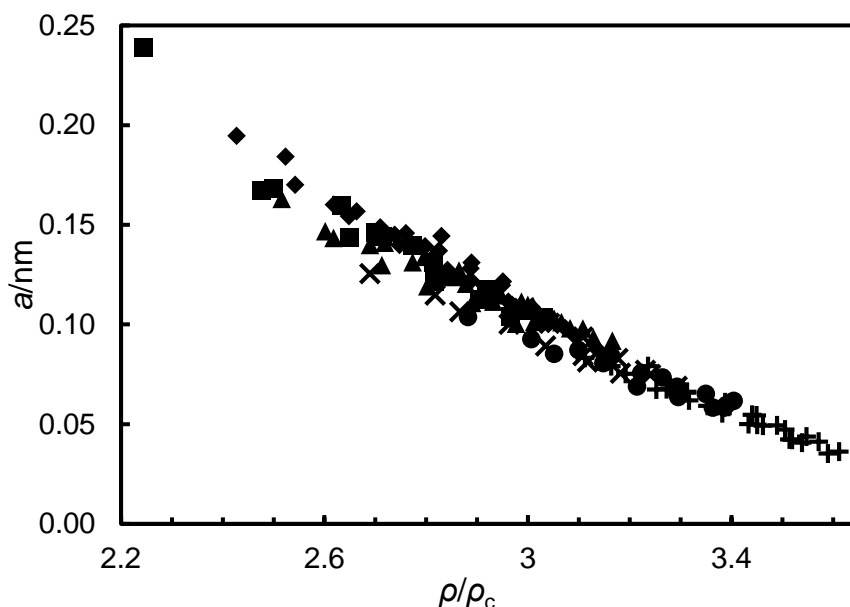


Figure 7. The fitted hydrodynamic radius of CO₂, a , plotted against the ratio of the solvent density at the respective temperature, ρ , and pressure to the critical density, ρ_c . The solvents under investigation were: ■, hexane; ◆, heptane; ▲, octane; ✕, decane; ●, dodecane and +, hexadecane.

In Figure 8 we compare the experimental diffusion coefficients for CO₂ in n-alkanes with the correlation based on the Stokes-Einstein equation with eq (16) for the hydrodynamic radius. The correlation fits the experimental data with an average absolute relative deviation, AAD, of

5 % and a maximum absolute relative deviation, MAD, of 19 %. The deviations are essentially independent of temperature but do show a slight positive bias with increasing pressure.

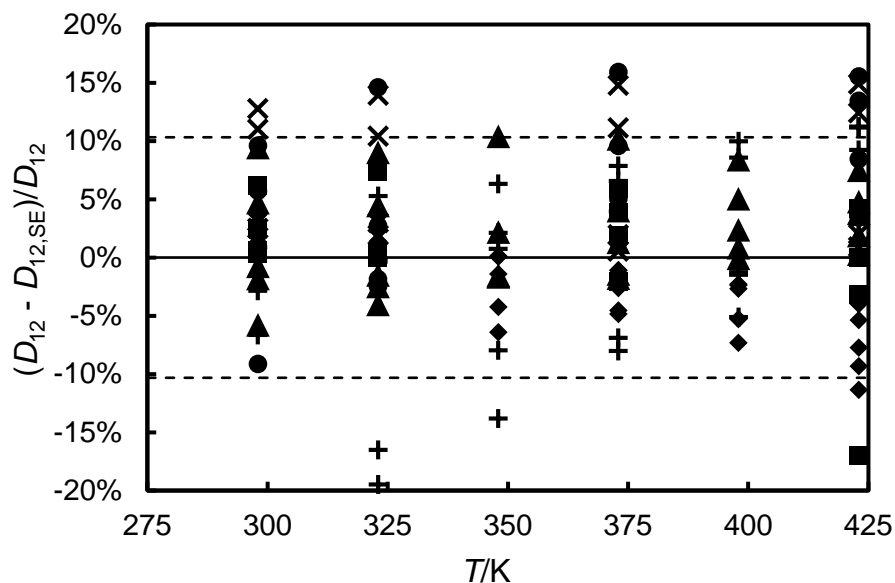


Figure 8. Deviation between the measured diffusion coefficients D_{12} of CO_2 in the homologous series of n-alkanes and values $D_{12,SE}$ predicted from the correlation based on the Stokes-Einstein equation as a function of temperature T . The solvents under investigation were: \blacksquare , hexane; \blacklozenge , heptane; \blacktriangle , octane; \times , decane; \bullet , dodecane and $+$, hexadecane. The dashed lines denote twice the standard deviation of the correlation.

The same analysis was attempted for CO_2 diffusion in squalane and the resulting hydrodynamic radii are plotted as a function of the solvent molar density in Figure 9, from which it is clear that such a simple approach is unsuccessful. We speculate that the flexibility of the molecule is responsible for the more complex behaviour of the apparent hydrodynamic radius of the solute.

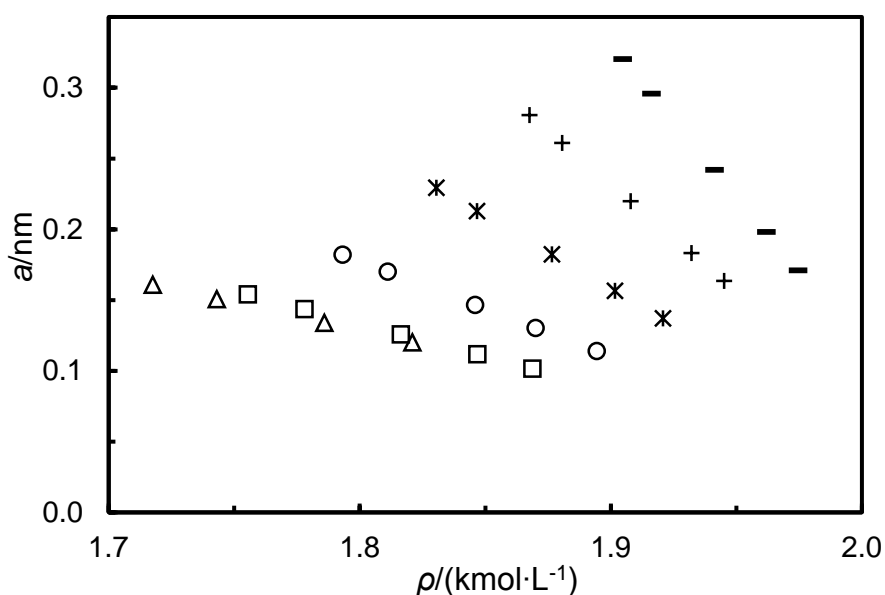


Figure 9. The hydrodynamic radius of CO_2 in squalane, a , plotted against the solvent density at each isotherm: $-$, $T = 298$ K; $+$, $T = 323$ K; $*$, $T = 348$ K; \circ , $T = 373$ K; \square , $T = 398$ K and \triangle , $T = 423$ K.

5. Rough-Hard-Sphere Model

To apply this model to the current results, the molar core volumes $V_{0,1}$ of CO_2 and $V_{0,2}$ of the hydrocarbon solvents were taken to be those obtained from application of rough-hard-sphere theory to the transport properties of the pure substances.^{24, 39, 40} Reduced diffusion coefficients could then be calculated according to equation 10 with trial values of the roughness factor. The MD results for smooth hard spheres interpolated to $M_1 V_{0,2}/(M_2 V_{0,1}) = 2.1$ were also included in the analysis with $A_{12} = 1$. Since $F_D^{(\text{CO}_2)}(V/V_{0,2})$ was to be determined from an analysis of the data, it was necessary to adopt a suitable functional form. Although the molecular dynamics results of Akgerman *et al.*^{28, 41} suggest a linear universal function, we find that D_{12}^* has a non-linear dependence on $V/V_{0,2}$, especially at $V/V_{0,2} < 1.3$. Accordingly, $F_D^{(\text{CO}_2)}(V/V_{0,2})$ was represented by a polynomial function as follows:

$$F_D^{(\text{CO}_2)}(V/V_{0,2}) = \sum_{i=0}^3 a_i (V/V_{0,2})^i . \quad (17)$$

The coefficients a_i and the roughness factors A_{12} for each solvent were then adjusted in a least squares analysis with an objective function based on relative deviation. The coefficients in eq (17) so determined are $a_0 = 2.8907$, $a_1 = -6.4199$, $a_2 = 4.47149$ and $a_3 = -0.9290$, and the correlation for $F_D^{(\text{CO}_2)}(V/V_{0,2})$ is valid for $1.18 \leq V/V_{0,2} \leq 2.00$. The roughness factors A_{12} are given in Table 11 along with the average absolute relative deviation Δ_{AAD} and maximum absolute relative deviation Δ_{MAD} for each solvent. We note that, for the alkanes, A_{12} appears to be a linear function of the reduced mass M_{12} . It is also notable that the data for ($\text{CO}_2 + \text{methylbenzene}$) fit the correlation just as well as for the ($\text{CO}_2 + \text{alkane}$) systems. Figure 10

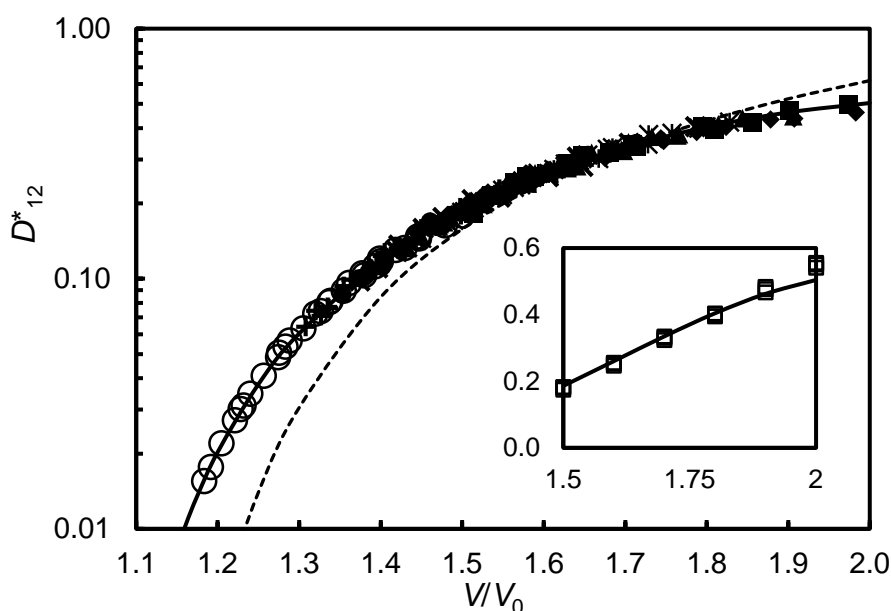


Figure 10. Correlation for the reduced mutual diffusion coefficient D_{12}^* of CO_2 in liquid hydrocarbon solvents as a function of reduced molar volume $V/V_{0,2}$, where $V_{0,2}$ is the molar core-volume of the pure solvent: ■, hexane; ◆, heptane; ▲, octane; ✕, decane; ●, dodecane; +, hexadecane; O, squalane; *, toluene; —, eq (17); - - -, universal correlation for self diffusion. Inset: □, molecular dynamics data interpolated to $M_1 V_{0,2}/(M_2 V_{0,1}) = 2.1$; —, eq (17).

shows the experimental reduced mutual diffusion coefficients in comparison with the new universal function on a semi-logarithmic scale. The inset compares the molecular dynamics data for smooth hard spheres with our correlation on a linear scale. It can be seen that the correlation agrees very well with the molecular dynamics data except at the largest reduced volume considered.

Figure 11 shows the relative deviations of the experimental diffusion coefficients from the new correlation, based on the rough-hard-sphere model, as a function of temperature. The average absolute relative deviation of the experimental data as a whole from the correlation was 2.5 % and the maximum absolute relative deviation was 8 %; these deviations are broadly consistent with the experimental uncertainties.

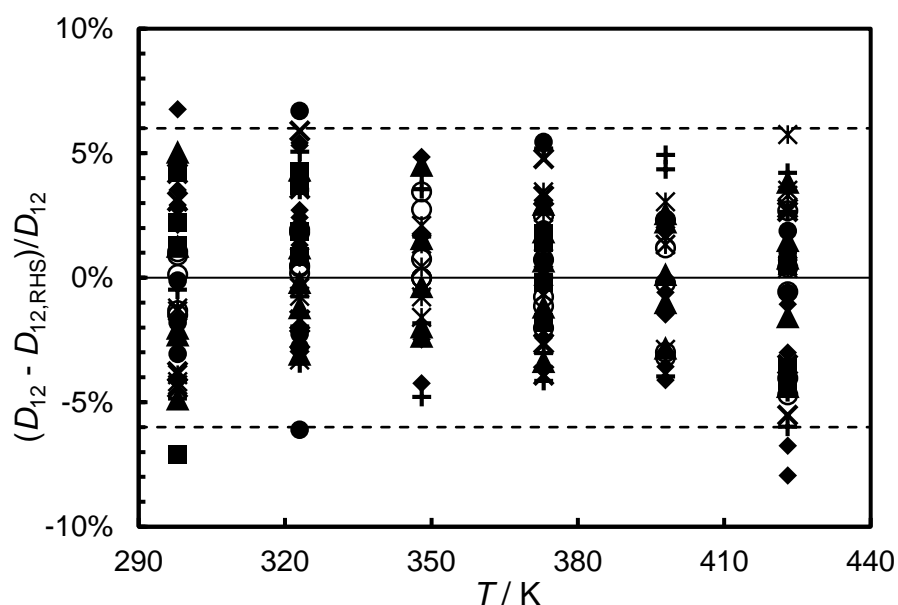


Figure 11. Deviation between the measured diffusion coefficients D_{12} of CO_2 in liquid hydrocarbon solvents from values $D_{12,\text{RHS}}$ predicted by the new correlation based on the rough-hard-sphere model at temperatures T : ■, hexane; ◆, heptane; ▲, octane; ✕, decane; ●, dodecane, +, hexadecane; ○, squalane; *, toluene. The dashed lines denote twice the standard relative deviation.

5. Conclusions

Measured diffusion coefficients of infinitely dilute CO_2 in a homologous series of n-alkanes and in methylbenzene and squalane were found to be strongly dependent upon pressure. A decrease of about 35 % over the pressure range of (0.1 to 69) MPa was noted for all cases except squalane, where the reduction was up to 55 % over the same pressure range. A correlation, based on the Stokes-Einstein equation, has been proposed for the diffusion coefficient of CO_2 in the six n-alkanes as a function of solvent viscosity and density and the temperature. This correlation has an average absolute deviation of 5 % from the measured data; however, the same approach is not successful for CO_2 diffusion in squalane. The rough hard sphere theory was found to perform much better and was used to represent all of the measured data with an average absolute relative deviation of 2.5 %. Our rough-hard-sphere

correlation should apply to CO₂ diffusion in any hydrocarbon solvent at high dilution of the CO₂. In addition to the molar core volume $V_{0,2}$, which may be obtained from viscosity data for the pure solvent, the model requires only the value of the roughness factor A_{12} , which may be determined from a single diffusion coefficient datum.

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Table 1. Description of Chemical Samples, Where x is Mole Fraction and w is Mass Fraction.

Chemical Name	Source	Purity as Supplied ^a	Additional Purification
Carbon dioxide	BOC	$x \geq 0.99995$	None
Hexane	Sigma Aldrich	$w \geq 0.97$	Degassed
Heptane	Sigma Aldrich	$w \geq 0.99$	Degassed
Octane	Sigma Aldrich	$w \geq 0.99$	Degassed
Decane	Sigma Aldrich	$w \geq 0.99$	Degassed
Dodecane	Sigma Aldrich	$w \geq 0.99$	Degassed
Hexadecane	Sigma Aldrich	$w \geq 0.99$	Degassed
2,6,10,15,19,23-hexamethyltetracosane (squalane)	Sigma Aldrich	$w \geq 0.99$	Degassed
Methylbenzene	Sigma Aldrich	$w \geq 0.999$	Degassed

^a Purities are as stated by the supplier.

Table 2: Diffusion Coefficients D_{12} of CO₂ in Hexane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.3 ^b	8.32
298	22 ^c	7.27
298	49 ^d	6.06
298	65 ^d	5.13
323	1.2 ^b	10.5
323	22 ^c	9.27
323	50 ^d	7.61
323	66 ^d	7.15
373	1.2 ^b	15.8
373	22 ^c	13.4
373	49 ^d	11.0
373	64 ^d	10.3
423	1.2 ^b	18.7
423	22 ^c	17.9
423	48 ^d	14.9
423	64 ^d	13.7

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 25 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 200 mm long restriction tube used

^d 25 μm i.d. x 500 mm long restriction tube used

Table 3. Diffusion Coefficients D_{12} of CO₂ in Heptane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.0 ^b	7.28
298	10 ^c	6.82
298	31 ^d	5.9
298	50 ^e	5.37
298	68 ^e	5.06
323	1.0 ^b	9.25
323	10 ^c	8.72
323	30 ^d	7.64
323	51 ^e	6.95
323	68 ^e	6.37
348	1.0 ^b	11.4
348	10 ^c	10.2
348	30 ^d	9.4
348	48 ^e	8.1
348	67 ^e	7.89
373	1.0 ^b	13.7
373	10 ^c	12.5
373	30 ^d	11.2
373	49 ^e	9.95
373	68 ^e	9.32
398	1.0 ^b	16.1
398	10 ^c	14.9
398	30 ^d	13.1
398	50 ^e	11.7
398	68 ^e	10.9
423	1.0 ^b	18
423	10 ^c	16.8
423	30 ^d	15
423	50 ^e	13.6
423	68 ^e	12.3

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 50 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 100 mm long restriction tube used

^d 25 μm i.d. x 200 mm long restriction tube used

^e 25 μm i.d. x 500 mm long restriction tube used

Table 4. Diffusion Coefficients D_{12} of CO₂ in Octane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.0 ^b	6.32
298	11 ^c	5.66
298	33 ^d	4.72
298	50 ^e	4.28
298	66 ^e	3.83
323	0.9 ^b	8.19
323	11 ^c	7.36
323	32 ^d	6.10
323	51 ^e	5.62
323	68 ^e	5.10
348	0.9 ^b	10.4
348	11 ^c	8.98
348	33 ^d	7.70
348	50 ^e	7.07
348	69 ^e	6.54
373	1.1 ^b	12.6
373	11 ^c	11.1
373	31 ^d	9.46
373	50 ^e	8.87
373	67 ^e	8.01
398	1.1 ^b	14.8
398	11 ^c	13.4
398	31 ^d	11.4
398	51 ^e	10.6
398	69 ^e	9.67
423	1.1 ^b	16.7
423	11 ^c	16.2
423	29 ^d	13.6
423	51 ^e	12.7
423	65 ^e	11.4

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 50 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 100 mm long restriction tube used

^d 25 μm i.d. x 200 mm long restriction tube used

^e 25 μm i.d. x 500 mm long restriction tube used

Table 5. Diffusion Coefficients D_{12} of CO₂ in Decane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.1 ^b	4.69
298	22 ^c	4.00
298	45 ^d	3.22
298	68 ^e	2.84
323	1.1 ^b	6.44
323	22 ^c	5.41
323	46 ^d	4.39
323	68 ^e	3.91
373	1.1 ^b	10.4
373	22 ^c	8.76
373	44 ^d	7.08
373	67 ^e	6.34
423	1.1 ^b	15.1
423	21 ^c	12.7
423	43 ^d	10.2
423	66 ^e	9.17

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 25 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 100 mm long restriction tube used

^d 25 μm i.d. x 200 mm long restriction tube used

^e 25 μm i.d. x 500 mm long restriction tube used

Table 6. Diffusion Coefficients D_{12} of CO₂ in Dodecane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.3 ^b	3.72
298	24 ^c	3.10
298	47 ^d	2.65
323	1.2 ^b	5.53
323	25 ^c	4.23
323	46 ^d	3.65
323	63 ^d	3.44
373	1.2 ^b	9.30
373	24 ^c	7.57
373	46 ^d	6.54
373	61 ^d	5.98
423	1.2 ^b	13.5
423	23 ^c	11.4
423	46 ^d	9.75
423	65 ^d	8.65

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 25 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 100 mm long restriction tube used

^d 25 μm i.d. x 500 mm long restriction tube used

Table 7. Diffusion Coefficients D_{12} of CO₂ in Hexdecane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2\cdot\text{s}^{-1})$
298	1.0 ^b	2.49
298	10 ^c	2.31
298	30 ^d	2.08
323	1.1 ^b	3.75
323	10 ^c	3.41
323	30 ^d	3.17
323	51 ^e	2.61
323	69 ^e	2.51
348	1.0 ^b	5.13
348	10 ^c	4.64
348	30 ^d	4.37
348	50 ^e	3.77
348	67 ^e	3.49
373	1.1 ^b	6.72
373	10 ^c	6.17
373	30 ^d	5.88
373	52 ^e	4.84
373	67 ^e	4.67
398	1.1 ^b	8.53
398	29 ^d	7.42
398	53 ^e	6.27
398	69 ^e	5.86
423	1.1 ^b	10.4
423	10 ^c	9.72
423	29 ^d	9.16
423	45 ^e	7.96
423	69 ^e	7.07

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 250 μm i.d. x 53 mm long restriction tube used

^c 50 μm i.d. x 100 mm long restriction tube used

^d 50 μm i.d. x 500 mm long restriction tube used

^e 25 μm i.d. x 200 mm long restriction tube used

Table 8. Diffusion Coefficients D_{12} of CO₂ in Squalane at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
298	1.1 ^b	0.96
298	10 ^c	0.86
298	32 ^d	0.69
298	52 ^d	0.56
298	66 ^d	0.49
323	1.1 ^b	1.78
323	10 ^c	1.61
323	30 ^d	1.35
323	52 ^d	1.14
323	64 ^d	1.02
348	1.0 ^b	2.83
348	11 ^c	2.57
348	31 ^d	2.18
348	50 ^d	1.94
348	67 ^d	1.73
373	1.0 ^b	4.06
373	10 ^c	3.72
373	30 ^d	3.21
373	47 ^d	2.88
373	66 ^d	2.58
398	1.0 ^b	5.45
398	11 ^c	4.98
398	31 ^d	4.38
398	50 ^d	3.89
398	66 ^d	3.55
423	1.0 ^b	7.01
423	11 ^c	6.36
423	30 ^d	5.69
423	50 ^d	5.00
423	67 ^d	4.60

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b no restriction tube used

^c 50 μm i.d. x 50 mm long restriction tube used

^d 50 μm i.d. x 100 mm long restriction tube used

Table 9. Diffusion Coefficients D_{12} of CO₂ in Methylbenzene at Temperatures T and Pressures p .^a

T/K	p/MPa	$D_{12}/(10^{-9} \text{ m}^2\cdot\text{s}^{-1})$
298	1.0 ^b	5.53
298	11 ^c	5.09
298	30 ^d	4.77
298	48 ^e	4.28
298	68 ^e	3.92
323	1.0 ^b	7.28
323	10 ^c	6.78
323	30 ^d	6.32
323	49 ^e	5.70
323	66 ^e	5.17
348	1.0 ^b	9.26
348	11 ^c	8.62
348	30 ^d	8.02
348	48 ^e	7.31
348	67 ^e	6.54
373	1.0 ^b	11.4
373	10 ^c	10.4
373	30 ^d	9.81
373	51 ^e	8.94
373	67 ^e	8.00
398	1.0 ^b	13.8
398	10 ^c	12.4
398	30 ^d	11.7
398	48 ^e	10.5
398	68 ^e	9.6
423	1.1 ^b	16.0
423	10 ^c	15.0
423	30 ^d	14.0
423	50 ^e	12.3
423	67 ^e	11.4

^a standard uncertainties are $u(T) = 0.01 \text{ K}$, $u(p) = 0.5 \text{ MPa}$ and $u(D_{12}) = 0.026 \cdot D_{12}$

^b 50 μm i.d. x 50 mm long restriction tube used

^c 25 μm i.d. x 150 mm long restriction tube used

^d 25 μm i.d. x 200 mm long restriction tube used

^e 25 μm i.d. x 500 mm long restriction tube used

Table 10. Coefficients D_0 and b in equation (15) and standard deviations $\sigma(D_{12})$ for CO_2 diffusion coefficients D_{12} in different hydrocarbon liquids at temperatures T .

T/K	$D_0/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$	b/MPa^{-1}	$\sigma(D_{12})/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1})$
Hexane			
298	8.52	0.0075	0.22
323	10.51	0.0061	0.18
373	15.76	0.0069	0.36
423	19.23	0.0052	0.65
Heptane			
298	7.19	0.0055	0.18
323	9.20	0.0055	0.13
348	11.07	0.0056	0.46
373	13.43	0.0057	0.34
398	15.88	0.0058	0.33
423	17.89	0.0056	0.18
Octane			
298	6.21	0.0075	0.15
323	7.98	0.0069	0.28
348	9.93	0.0065	0.46
373	12.17	0.0066	0.52
398	14.41	0.0061	0.53
423	16.85	0.0060	0.45
Decane			
298	4.69	0.0077	0.14
323	6.40	0.0075	0.19
373	10.37	0.0078	0.36
423	15.02	0.0079	0.59
Dodecane			
298	3.74	0.0075	0.03
323	5.38	0.0078	0.30
373	9.22	0.0074	0.21
423	13.52	0.0070	0.16
Hexadecane			
298	2.48	0.0060	0.04
323	3.70	0.0060	0.14
348	5.06	0.0056	0.13
373	6.69	0.0056	0.23
398	8.20	0.0049	0.46
423	10.45	0.0057	0.24
Squalane			
298	0.97	0.0114	0.04
323	1.77	0.0086	0.02
348	2.80	0.0074	0.05
373	4.01	0.0069	0.07
398	5.40	0.0065	0.07
423	6.91	0.0063	0.12
Methylbenzene			
298	5.48	0.0050	0.09
323	7.26	0.0051	0.10
348	9.25	0.0051	0.11
373	11.26	0.0049	0.28
398	13.50	0.0051	0.35
423	16.01	0.0051	0.24

Table 11. Rotational-Translational Coupling Factors (Roughness Factor) A_{12} of CO_2 in Different Hydrocarbon Solvents Together With Average Absolute Relative Deviations Δ_{AAD} and Maximum Absolute Relative Deviations Δ_{MAD} of the Experimental Diffusion Coefficients From the Rough-Hard-Sphere Model.

Solvent	A_{12}	$10^2\Delta_{\text{AAD}}$	$10^2\Delta_{\text{MAD}}$
Hexane	0.914	2.7	7.1
Heptane	0.917	3.0	7.9
Octane	0.847	2.2	5.1
Decane	0.779	3.6	5.9
Dodecane	0.761	2.3	6.7
Hexadecane	0.706	3.4	6.0
Squalane	0.520	1.5	4.7
Methylbenzene	1.060	2.1	5.8