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Infinite Dilution Binary Diffusion Coefficients of Hydrotreating Compounds in Tetradecane in the Temperature Range from (310 to 475) K

Nathalie Márquez, Michiel T. Kreutzer, Michiel Makkee,* and Jacob A. Moulijn

Catalysis Engineering, Delft University of Technology, Julianalaan 136, NL 2628 BL Delft, The Netherlands

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Infinite dilution diffusion coefficients of benzothiophene, dibenzothiophene, acridine, naphthalene, and anthracene in tetradecane have been measured in a temperature range from (313.2 to 473.2) K using the Taylor dispersion technique. Predicted values based on the correlations of Wilke−Chang and Tyn−Calus deviate up to 35 %. An Arrhenius type of equation was used to describe the temperature dependence of the diffusion coefficients with an accuracy on average of less than 5 %.

Introduction

Accurate values of diffusivity are essential in the description and modeling of chemical reactors, especially in those processes where slow diffusion of large molecules in the micropores of a porous catalyst can limit the reaction rate. For the deep hydrodesulfurization (HDS) toward "ultra-low" sulfur levels, diffusion might play an increasingly important role for the optimal performance of the HDS process.[1]

There are no data available for the infinite dilution binary diffusion coefficients D_{12} of the large aromatic, diesel-like compounds, in long chain alkanes. In practice, these diffusion coefficient values are estimated using published correlations like the Wilke−Chang[2] or the Tyn–Calus (modified by Reid) correlation.[3,4]

Other authors have reported diffusivity values for similar solute–solvent combinations using the Taylor dispersion technique.[5] Fan et al.[6] determined the diffusion coefficients of benzene, naphthalene, diphenyl, anthracene, and phenanthrene in heptane and octane in a temperature range from (303.2 to 333.2) K with standard deviations less than 5 %. Safi et al.[7] reported the diffusivity value of naphthalene in hexane, heptane, octane, and decane at 298.2 K with uncertainties around 1 %. In the present study, the infinite dilution D_{12} values of benzothiophene, dibenzothiophene, acridine, naphthalene, and anthracene in tetradecane were determined in a temperature range from (313.2 to 473.2) K using the Taylor dispersion method. D_{12} values with standard deviations smaller than 3 % are presented, and an experimental correlation is postulated.

Experimental Section

Chemicals. Benzothiophene, naphthalene, and anthracene were obtained from Aldrich with 99 % purity. Tetradecane was obtained from Acros Organics with a purity of 99 %. Dibenzothiophene and acridine were obtained from Aldrich with purities of 98 % and 97 %, respectively. All chemicals were used without further purification.

Taylor Dispersion Apparatus. The experimental apparatus is described schematically in Figure 1. The measurement was based on injecting a pulse of a dilute solution into a tube and determining the spread of the solute pulse leaving the tube. The setup consisted of a syringe pump (ISCO, model 500D), which delivered tetradecane flow rates between (0.15 and 0.30) mL·min^{-1}. The pump was connected to an HPLC injection valve (Rheodyne, model 7725) with a sample volume of 10 μL. All samples were prepared as dilute solutions of the tracer in tetradecane with mole fractions less than 1 %. A long capillary helically coiled fused silica tubing (BGB Analytik AG) was directly attached to the injection valve. The tube had a length of (13.926 ± 0.001) m and an internal diameter of (0.530 ± 0.012) mm. The diameter of the coil was 0.40 m. 90 % of the capillary length was inside an oven that controlled the temperature to 1 K. A refractive index detector (RI2000 Schambeck SFD GmbH) was directly attached to the capillary. The differential refractometer continuously measured the difference in refractive index between the sample stream and the reference liquid stream. A LabVIEW program was used to store the data on a PC with a sampling frequency of 1 Hz.

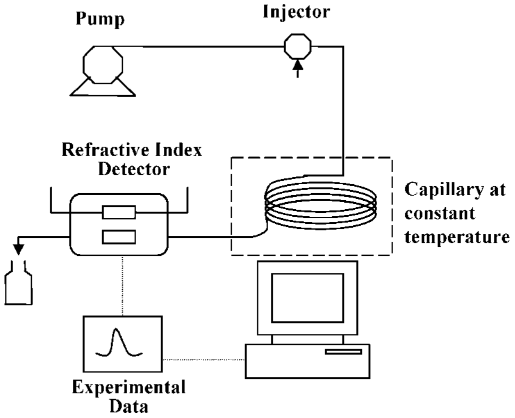

Figure 1. Experimental setup for the measurement of diffusion coefficients with the Taylor dispersion technique.

Diffusivity Value Determination. Taylor, later extended by Aris[8] to include axial diffusion, derived an expression for the variance of the distribution of elution time of the injected tracer (for details, see refs 5 and 8).

$$\sigma^2/s^2 = \frac{\tau r^2}{24 D_{12}} \tag{1}$$

in which σ^2 is the second moment of the elution time distribution (the variance); τ is the first moment of the elution time

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* Corresponding author. Tel.: +31 15 278 1391. Fax: +31 15 278 5006. E-mail address: m.makkee@tudelft.nl.

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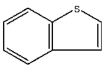
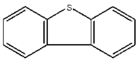
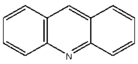
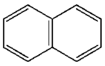
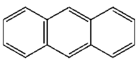
Table 1. Determined Variance for the Total System $\sigma^2_{\mathrm{total}}$[a], Variance for the Inlet and Outlet Sections $\sigma^2_{\mathrm{i-o}}$[a], and Infinite Dilution Binary Diffusion Coefficients D_{12}[a] with Calculated Tetradecane Viscosity η[b] and DeSc$^{1/2}$[c] Values for Benzothiophene, Dibenzothiophene, Acridine, Naphthalene, and Anthracene on Tetradecane

Solute	T/K	η/10^{-4} Pa·s	σ^2_{total}/s^2	σ^2_{i-o}/s^2	D_{12}/10^{-9}m^2·s^{-1}	$DeSc^{1/2}$
Benzothiophene	333.2	11.51	2576.13(107.66)	484.00(0)	1.19(7)	6.64(40)
	353.2	8.76	1958.13(31.29)	484.00(0)	1.65(3)	6.48(39)
	373.2	6.92	1620.63(85.38)	484.00(0)	2.10(16)	6.55(39)
	393.2	5.63	1425.13(26.69)	484.00(0)	2.51(7)	6.60(39)
	413.2	4.67	798.13(19.98)	315.13(12.55)	3.19(13)	9.80(46)
	423.2	4.28	715.63(18.92)	315.13(12.55)	3.83(19)	9.33(43)
	453.2	3.35	625.00(0)	315.13(12.55)	4.77(2)	9.55(44)
Dibenzothiophene	333.2	11.51	2970.25(0)	612.63(17.50)	1.06(0)	7.16(43)
	353.2	8.76	2352.25(0)	612.63(17.50)	1.41(0)	7.05(42)
	393.2	5.63	1722.50(58.69)	612.63(17.50)	2.13(10)	7.01(42)
	413.2	4.67	961.00(0)	371.13(20.84)	2.61(1)	10.30(49)
	423.2	4.28	855.63(20.68)	371.13(20.84)	3.14(13)	9.75(46)
	433.2	3.94	812.25(0)	371.13(20.84)	3.41(1)	9.70(46)
	453.2	3.35	742.63(19.27)	371.13(20.84)	3.96(19)	9.64(46)
	463.2	3.10	663.13(18.21)	371.13(20.84)	5.01(31)	8.86(42)
Acridine	333.2	11.51	2500.25(70.71)	540.63(16.44)	1.27(5)	6.91(42)
	353.2	8.76	2116.25(65.05)	540.63(16.44)	1.55(7)	7.11(43)
	373.2	6.92	1736.17(24.10)	540.63(16.44)	2.00(4)	6.95(42)
	393.2	5.63	1521.17(39.00)	540.63(16.44)	2.40(10)	6.96(42)
	413.2	4.67	841.25(41.01)	315.13(12.55)	2.93(21)	10.26(50)
	423.2	4.28	729.25(38.18)	315.13(12.55)	3.74(36)	9.43(46)
	453.2	3.35	689.13(18.56)	315.13(12.55)	3.96(18)	10.16(50)
	473.2	2.87	600.50(34.65)	315.13(12.55)	5.08(60)	9.57(47)
Naphthalene	313.2	15.90	2862.50(75.66)	400.25(18.28)	1.03(3)	6.23(38)
	333.2	11.51	2162.25(0)	400.25(18.28)	1.42(0)	6.19(37)
	353.2	8.76	1722.25(0)	400.25(18.28)	1.86(1)	6.13(37)
	373.2	6.92	1463.13(27.05)	400.25(18.28)	2.28(6)	6.17(37)
	418.2	4.47	1024(0)	400.25(18.28)	3.69(0)	5.89(35)
	433.2	3.94	600.25(0)	272.25(0)	4.64(1)	8.32(40)
	453.2	3.35	540.63(16.44)	272.25(0)	5.56(32)	8.14(39)
Anthracene	333.2	11.51	3249.25(80.61)	600.25(0)	0.94(3)	7.60(52)
	353.2	8.76	2401(0)	600.25(0)	1.36(0)	7.17(49)
	373.2	6.92	2328.13(34.12)	600.25(0)	1.38(3)	7.92(54)
	393.2	5.63	1764(0)	600.25(0)	2.03(0)	7.17(49)
	433.2	3.94	870.25(0)	430.63(14.67)	3.43(1)	9.68(56)
	443.2	3.63	756.25(0)	430.63(14.67)	4.57(1)	8.68(50)

[a] The standard deviation, determined from three measurements, is given in parentheses. [b] The tetradecane viscosity was estimated using the correlation published by Yaws.[13] [c] The estimated error is given in parenthesis.

distribution (the mean residence time, s); r is the internal radius of the capillary; and D_{12} is the diffusivity value of the solute (1) in the solvent (2).

Taylor demonstrated that the elution curve was a Gaussian distribution, from which the first and second moments (τ and σ^2) can be determined. For each peak, the first moment was estimated as the retention time at the maximum peak height and the spread (i.e., 2σ) was estimated as the peak width at a 61 % of this maximum peak height.[9]

To eliminate the contribution to the tracer dispersion due to sections outside the capillary column inside the oven, experiments were also performed with a short-cut capillary, which connects the injection valve to the refractometer bypassing the oven. The mean residence time and the variance for the peak obtained with the shorter column were calculated using the same approach as for the long capillary. In this way, a correction is made for the input and output effects according to the following formulas:

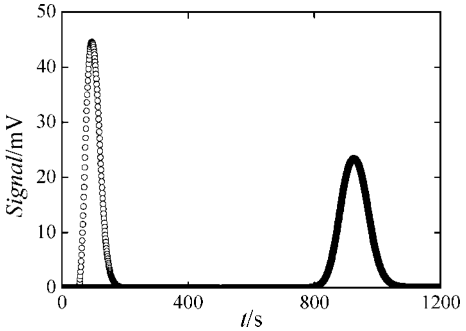


Figure 2. Dispersion peaks using the refractive index detector. ○, inlet and outlet sections; ●, total setup. Benzothiophene (1) in tetradecane (2) at 353.2 K. Tracer feed concentration $x_1 = 0.38$ %.

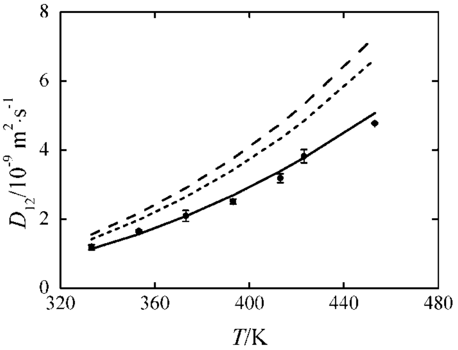


Figure 3. Infinite dilution binary diffusion coefficients D_{12} as a function of temperature T. ●, This work, with error bars representing the standard deviation; - -, predicted D_{12} values according to Wilke−Chang; --, predicted D_{12} values according to the Tyn–Calus correlation; —, predicted D_{12} values with a correlation based on the Arrhenius activation energy. System: Benzothiophene in tetradecane.

$$\tau_{\text{capillary}} = \tau_{\text{total}} - \tau_{\text{i-o}} \tag{2}$$

$$\sigma^2_{\text{capillary}} = \sigma^2_{\text{total}} - \sigma^2_{\text{i-o}} \tag{3}$$

where subscripts capillary, total, and i−o refer to the capillary section inside the oven, the total setup, and the inlet and outlet sections, respectively.

Set-up Restrictions. The assumptions made in the derivation of 1 impose some constraints on the experimental conditions:

1. The analysis assumes laminar flow. The experimental range of the Reynolds number (Re) was from 3 to 32, indicating laminar flow conditions.

2. The diffusion coefficient is assumed to be independent of concentration and equal to the value at infinite dilution. Varying the tracer concentration until a maximum mole fraction of 1 %, the effect on σ^2 was less than 2.5 %; therefore, the tracer concentration effect can be neglected.

3. Axial molecular diffusion is neglected in the Taylor analysis. Alizadeh[10] demonstrated analytically that the effect on σ^2 is less than 0.01 % when the Peclet number ($\mathrm{Pe} = uL/D_{12}$) is larger than $700L/r$, where L is the capillary length and u is the fluid velocity. Furthermore, the radial concentration differences are assumed to be small. Alizadeh[10] has found that the error in σ^2 is less than 0.01 % when $\mathrm{Pe} < 0.1L^2/r^2$. Experimental values of Pe varied between $4.45 \cdot 10^7$ and $2.31 \cdot 10^8$. Both the axial and radial restrictions have been fulfilled.

4. For practical reasons the capillary has to be coiled. Janssen[11]demonstrated that for Dean numbers $\left(\mathrm{De} = \mathrm{Re}\sqrt{r/r_c}\right) < 16$ and for $r_c/r > 20$, where r_c is the radius of the coil, the secondary flow due to coiling does not have a significant effect, when the group $\mathrm{De}\sqrt{\mathrm{Sc}}$ is smaller than 10 (where Sc is the Schmidt number). Our experimental values of De are smaller than 1; the ratio r_c/r is 1509; and the $\mathrm{De}\sqrt{\mathrm{Sc}}$ values (shown in Table 1) indicate that the error in our results due to coiling is less than 3 %.

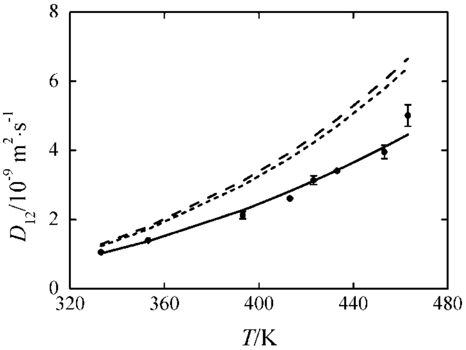


Figure 4. Infinite dilution binary diffusion coefficients D_{12} as a function of temperature T. ●, This work, with error bars representing the standard deviation; - -, predicted D_{12} values according to Wilke–Chang; --, predicted D_{12} values according to the Tyn–Calus correlation; —, predicted D_{12} values with a correlation based on the Arrhenius activation energy. System: Dibenzothiophene in tetradecane.

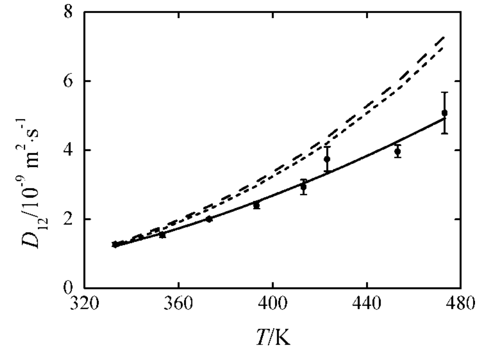


Figure 5. Infinite dilution binary diffusion coefficients D_{12} as a function of temperature T. ●, This work, with error bars representing the standard deviation; - -, predicted D_{12} values according to Wilke−Chang; --, predicted D_{12} values according to the Tyn–Calus correlation; —, predicted D_{12} values with a correlation based on the Arrhenius activation energy. System: Acridine in tetradecane.

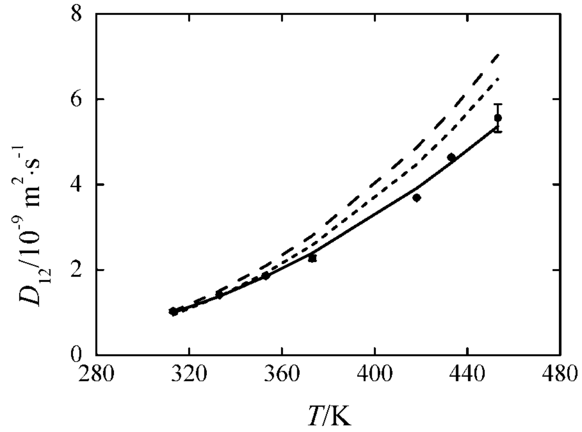


Figure 6. Infinite dilution binary diffusion coefficients D_{12} as a function of temperature T. ●, This work, with error bars representing the standard deviation; - -, predicted D_{12} values according to Wilke−Chang; --, predicted D_{12} values according to the Tyn–Calus correlation; —, predicted D_{12} values with a correlation based on the Arrhenius activation energy. System: Naphthalene in tetradecane.

Curve Shape. Figure 2 shows representative curves of the raw reading in the refractive index meter for the short capillary

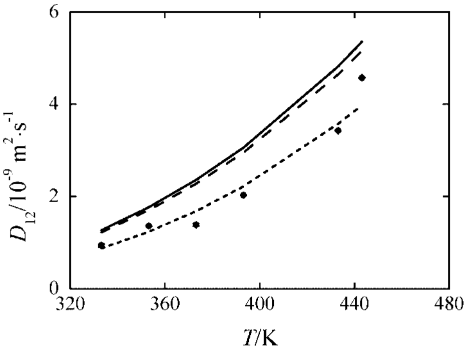


Figure 7. Infinite dilution binary diffusion coefficients D_{12} as a function of temperature T. ●, This work, with error bars representing the standard deviation; - -, predicted D_{12} values according to Wilke−Chang; --, predicted D_{12} values according to the Tyn–Calus correlation; —, predicted D_{12} values with a correlation based on the Arrhenius activation energy. System: Anthracene in tetradecane.

(setup inlet and outlet sections) and the long capillary. The elution curve for the total system is Gaussian, as predicted. The elution curve for the inlet and outlet setup sections shows some tailing, but the error in the second moment evaluation for this curve is less than 4.5 %.

Experimental Errors. The temperature range of the experiments was selected to guarantee that the experimental temperature is at least 20 K below the boiling point of the solute and the solvent, so evaporation effects can be neglected. The composite absolute error of each measurement was estimated by taking the root of the squares of the most significant experimental error contributions in the determination of the mean elution time, the capillary radius, and the peak width, according to

$$\Delta D_{12} = \sqrt{\left[\Delta\tau_{\text{capillary}}\cdot\left(\frac{\partial D_{12}}{\partial\tau_{\text{capillary}}}\right)\right]^2 + \left[\Delta R\cdot\left(\frac{\partial D_{12}}{\partial R}\right)\right]^2 + \left[\Delta\sigma^2_{\text{capillary}}\cdot\left(\frac{\partial D_{12}}{\partial\sigma^2_{\text{capillary}}}\right)\right]^2} \quad (4)$$

where Δ stands for the experimental error in the variable value and $\partial D_{12}/\partial x$ is an indication of how much the diffusivity value varies when the variable x varies. The predicted error of the measurements was less than 4 %.

Results and Discussion

Table 1 shows the experimental D_{12} values obtained for each studied compound in tetradecane. The D_{12}value reported is the average of three measurements with the standard deviation. The standard deviation is defined as

$$\text{SDV} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \quad (5)$$

where n is the number of experimental points and $\bar{x}$ is the average value of the variable.

In general, the standard deviation is smaller than 3 %; only for the system acridine in tetradecane, the standard deviation is 6 %. The values of the second moment for the total system and for the inlet and outlet setup sections are also included in Table 1, because the evaluation of these parameters is the most critical factor in terms of accuracy.

The experimental values obtained are compared with the values predicted from the Wilke−Chang and modified Tyn−Calus correlations (see Figures 3 to 7). The predicted values derived from the generally accepted Wilke−Chang and modified Tyn−Calus correlations are, at 373.2 K, a factor 1.3 higher than the experimental values. These correlations are based on the Stokes–Einstein equation[12]

$$\frac{D_{12}\eta_2}{kT}/\text{m}^{-1} = \frac{1}{6\pi R_1} \quad (6)$$

where T is the absolute system temperature; η_2 and D_{12} are the solvent viscosity and diffusivity at that temperature; k is the Boltzmann constant; and R_1 is the solute molecular diameter. The tetradecane viscosity at different temperatures was estimated using the correlation published by Yaws,[13] and the calculated values are reported in Table 1.

The Stokes–Einstein model assumes that the molecules are hard spheres which have a diameter that remains unchanged with temperature variations; therefore, the relation $\eta D_{12}/T$ should be constant. We found that the $\eta D_{12}/T$ values decrease with temperature; i. e., the value of $\eta D_{12}/T$ for acridine at 333.2 K is 42 % higher than the value at 473.2 K. Thus, the Stokes–Einstein model does not represent the data behavior over the temperature range studied in this work, overestimating the diffusivity values at high temperatures.

The experimental data were correlated using Arrhenius' law,[9] reading:

$$D_{12} = A_{0,D}\cdot\exp\left(-\frac{E_{A,D}}{RT}\right) \quad (7)$$

where $A_{0,\text{D}}$ is a pre-exponential factor for diffusion; $E_{\text{A,D}}$ is an activation energy; and R is the gas constant. While physically diffusion in liquids is not thought to proceed through an activated state, the Arrhenius type of equation fits the data well because the viscosity exhibits an exponential temperature dependence. We fitted tabulated data of viscosity within the experimental temperature range to an Arrhenius type of equation to find a near perfect fit with $E_{\text{A},\eta}$ = –12.9 kJ·mol^{-1}. The product ηD_{12} varies much less with temperature, as expected based on the Stokes–Einstein equation.

The fitted pre-exponential factors and the activation energies for the systems analyzed are reported in Table 2. The goodness of the fit is indicated by the average fractional relative deviations between the diffusivity values measured experimentally and calculated by the fitted correlation. The average fractional relative deviation is smaller than 5 %; only for the system

Table 2. Pre-Exponential Factors $A_{0,\text{D}}$ and Activation Energies $E_{\text{A,D}}$ for Benzothiophene, Dibenzothiophene, Acridine, Naphthalene, and Anthracene in Tetradecane[a]

solute	T/K	$A_{0,\text{D}}$ / 10^{-7} m^2·s^{-1}	$E_{\text{A,D}}$ / kJ·mol^{-1}	100 / $n\cdot\Sigma\Delta D_{12}/D_{12}$
Benzothiophene	333.2 to 453.2	2.2 ± 0.7	14.5	2.6
Dibenzothiophene	333.2 to 463.2	2.0 ± 0.9	14.6	4.6
Acridine	333.2 to 473.2	1.4 ± 0.7	13.0	4.6
Naphthalene	313.2 to 453.2	2.3 ± 0.6	14.2	3.4
Anthracene	333.2 to 443.2	3.9 ± 0.9	16.9	9.5

[a] Average fractional relative deviations $100/n\cdot\Sigma(D_{12}\text{exptl} - D_{12}\text{calcd})/D_{12}\text{exptl}$ are also reported.

anthracene in tetradecane, the average fractional relative deviation is smaller than 10 %.

Conclusions

We report infinite dilution binary diffusion coefficients in the liquid phase using the Taylor dispersion method over a temperature range from (313.2 to 473.2) K for benzothiophene, dibenzothiophene, acridine, naphthalene, and anthracene in tetradecane.

Generally used correlations can over predict the diffusivity values at temperatures higher than 373 K. The experimental data were correlated using the Arrhenius law.

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