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High-Temperature Diffusion, Viscosity, and Density Measurements in *n*-Hexadecane

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Mutual diffusion coefficients at infinite dilution have been measured for *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane in the solvent *n*-hexadecane. The data cover the elevated temperature range 50–291 °C at pressures of 1415 and 3450 kPa (205 and 500 psia). Viscosity and density of the solvent were also measured at all conditions. The Taylor dispersion method was used for diffusion measurements, and a capillary tube viscometer for viscosity measurements. Densities were measured by using a new technique based on retention times observed in the Taylor dispersion experiment. A free-volume expression represents the diffusion data well across the entire temperature range.

Introduction

Mutual diffusion, viscosity, and density are the thermophysical properties needed in evaluation of mass transport phenomena. For high-temperature applications such as multiphase chemical reactors the need for data, particularly on diffusion, is acute. The objective of this work was to measure these three properties at temperatures to 291 °C and pressures to 3450 kPa, the range of conditions useful for many chemical processes. The *n*-hexadecane/alkane systems studied are important from a fundamental standpoint and also because of the industrial importance of hydrocarbon processing.

Experimental Techniques

Mutual diffusion coefficients of four *n*-alkane solutes (octane, decane, dodecane, and tetradecane) were measured by using the Taylor dispersion method (*1*). In this method, a narrow pulse of solute (A) diluted in the solvent (B) is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance σ^2 is dependent on the average flow velocity $\bar{u}$ and molecular diffusivity D_{AB}. At the end of the diffusion tube one records concentration $C(t)$ vs. time data as the peak elutes. The normalized first and second temporal moments ($\bar{t}$ and σ^2) are calculated by finite summation, and then the diffusion coefficient is calculated from eq 1

$$D_{AB} = \tfrac{1}{2}\left[\bar{u}L\zeta_0 - \left[(\bar{u}L\zeta_0)^2 - \left(\frac{\bar{u}^2R^2}{12}\right)\right]^{1/2}\right] \qquad (1)$$

where

$$\bar{u} = (L/\bar{t})\,(1 + 2\zeta_0) \qquad (2)$$

$$\zeta_0 = \frac{2\sigma^2 - \bar{t}^2 + [\bar{t}^4 + 4\bar{t}^2\sigma^2]^{1/2}}{(8t^2 - 4\sigma^2)} \qquad (3)$$

Equation 1 accounts for molecular diffusion in both axial and radial directions within the dispersion tube. The tube length L and radius R are corrected for thermal expansion effects which are significant at temperatures above 100 °C.

Viscosity is measured by using the standard capillary viscometer technique, which is based on the Hagen–Poiseuille equation. Density is measured by using a new technique based on the retention time of the solute peak (*2*, *3*). The retention time is just the first temporal moment $\bar{t}$ calculated from the Taylor dispersion experiment and it depends on the solvent density, dispersion tube volume V_t, and mass flow rate. We calibrated the tube volume using water at 30 °C (condition 1) and calculate the density of hexadecane at any other condition 2 as follows:

$$\rho_2 = \rho_1 \frac{\dot{m}^{(2)}}{\dot{m}^{(1)}} \frac{\bar{t}^{(2)}}{\bar{t}^{(1)}} \frac{V_t^{(1)}}{V_t^{(2)}} \qquad (4)$$

The tube volume $V_t^{(2)}$ is corrected for thermal expansion effects (*3*).

The apparatus is shown in Figure 1. The hexadecane solvent is sparged with helium and pumped through a capillary restrictor and backpressure regulator, which act to dampen pulses from the metering pump. The solvent flows into a heated enclosure which contains the stainless steel capillary viscometer. The capillary diameter was calibrated by using distilled, deionized water at 30 and 120 °C. The capillary length and diameter were corrected for thermal expansion. Pressure drop was measured with two strain gauge transducers which were calibrated against a Ruska Instruments dead-weight pressure gauge. With the aid of a valve manifold, each transducer was used to measure both upstream and downstream pressure, and pressure difference was calculated for each transducer. The pressure drop from the two transducers always agreed to 1% or less. The volumetric flow rate was determined by measuring the mass flow rate and density at each experimental condition.

After the viscometer, solvent flows through the reference side of the concentration detector (LDC/Milton Roy Refracto-

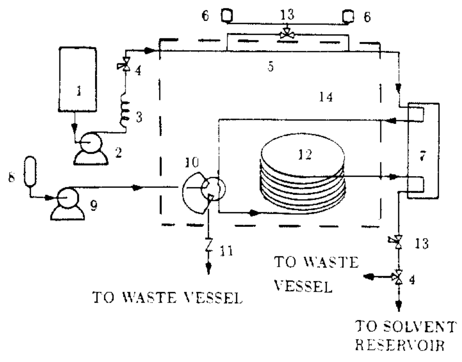

Figure 1. Schematic diagram of the Taylor dispersion apparatus with capillary viscometer: 1, solvent reservoir; 2, solvent pump; 3, capillary tube pulse damper; 4, backpressure regulators; 5, capillary tube viscometer; 6, pressure transducers; 7, refractive index detector; 8, sample solution; 9, sample injection pump; 10, 6-port sample injection valve; 11, adjustable check valve; 12, coiled dispersion tube; 13, 3-way valves; 14, heated enclosure.

Table I. Diffusion Coefficients of Alkanes in *n*-Hexadecane ($D_{AB} \times 10^9$ m^2/s)

T, °C	P, kPa	n-C_8	n-C_{10}	n-C_{12}	n-C_{14}
50	1439	1.15 ±0.03	1.01 ±0.02	0.94 ±0.02	0.85 ±0.03
50	3505	1.16 ±0.03			
98	1421	2.39 ±0.01	2.07 ±0.03	1.98 ±0.09	1.78 ±0.09
98	3490	2.42 ±0.03			
170	1416	5.11 ±0.03	4.4 ±0.04	4.01 ±0.10	3.55 ±0.20
170	3470	5.09 ±0.05			
240	1431	9.23 ±0.30	8.28 ±0.38	7.13 ±0.11	6.55 ±0.33
240	3473	8.71 ±0.22			
291	1422	12.8 ±0.1	11.7 ±0.3	10.0 ±0.3	9.46 ±0.42
291	3454	12.6 ±0.1			

monitor) and back into the heated enclosure, where the solute sample is injected. The sample was 8 mol % solute dissolved in hexadecane, and the sample was sparged with helium before injection into the dispersion tube. The dispersed peak then passed through the sample side of the detector and out of the system. Previous tests (*5*) have shown that the diffusion coefficient observed is independent of sample concentration at concentrations below 15 mol %.

Hexadecane and decane were obtained from Alfa Chemicals, octane and tetradecane from MCB Reagents, and dodecane from Eastman Chemicals. All were used as received. The minimum purity for all alkanes was 99 mol %, which was confirmed by gas chromatography.

Results and Discussion

Diffusion coefficients with the standard deviations are given in Table I. For each diffusivity, three repeat experiments were performed and the results were averaged. All previous measurements of mutual diffusion in hexadecane were taken below 100 °C, so this work represents a significant extension of the available data. As shown in Figure 2, a free volume expression (eq 5) fits the data well; values of β for each solute are given in Table II. The values of β can be correlated with solute molecular weight (*4*).

$$\frac{D_{AB}}{T^{1/2}} = \beta(V - 289.9) \qquad (5)$$

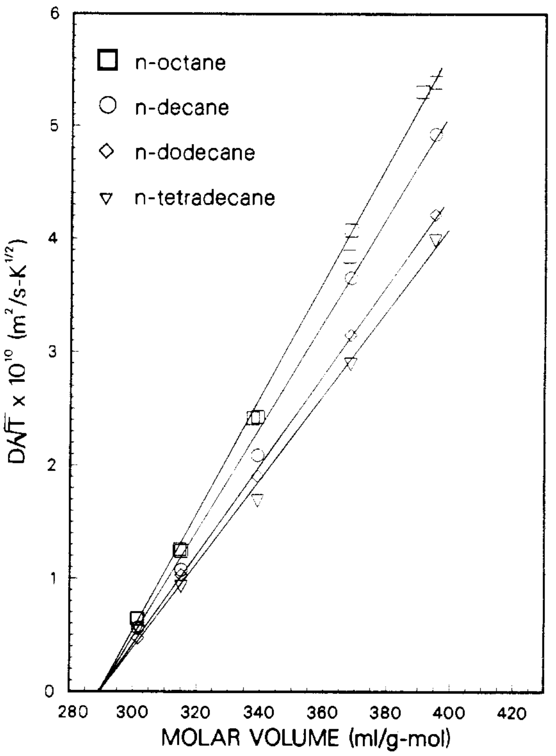

Figure 2. Free-volume relationship for mutual diffusion of *n*-alkane solutes in *n*-hexadecane. Solid lines are the correlation of eq 5.

Table II. Multiplier β for Diffusion of *n*-Alkanes in *n*-Hexadecane (Eq 5)

solute	β	solute	β
n-octane	0.005 16	*n*-dodecane	0.003 98
n-decane	0.004 75	*n*-tetradecane	0.003 77

Table III. Density and Viscosity of *n*-Hexadecane

T, °C	P, kPa	ρ, g/cm^3	η, cP
50	1439	0.7528	1.89
50	3505	0.7536	1.92
98	1421	0.7203	0.949
98	3490	0.7216	0.953
170	1416	0.6693	0.459
170	3470	0.6725	0.478
240	1431	0.6162	0.275
240	3473	0.6171	0.278
291	1422	0.5748	0.195
291	3454	0.5811	0.214

The constant 289.9 cm^3/g-mol is the theoretical molar volume at which diffusion would go to zero, and (V – 289.9) is the free volume.

Solvent viscosity and density are given in Table III. A correlation for *n*-hexadecane density as a function of pressure and temperatures to 125 °C has been given by Orwall and Flory (*6*), and our data agree to within 0.2% of that correlation at temperatures below 125 °C. The density measurements at 205 psia are shown in Figure 3 along with the correlation of Orwall and Flory (*5*). This work thus provides a modest extension of available data and also demonstrates the utility of the new density measurement technique. The accuracy of density measurements is estimated to be ±0.2%.

Viscosity data for *n*-hexadecane at saturation pressure and temperatures to 285 °C have been reported (*7*) but this work provides some additional information on the pressure dependence. The accuracy of the data is estimated to be ±3%.

In addition it is worthwhile to note that the experimental technique measures density, viscosity, and diffusion coefficients simultaneously; hence it allows calculation of the Schmidt number for mass-transfer correlations at temperatures and

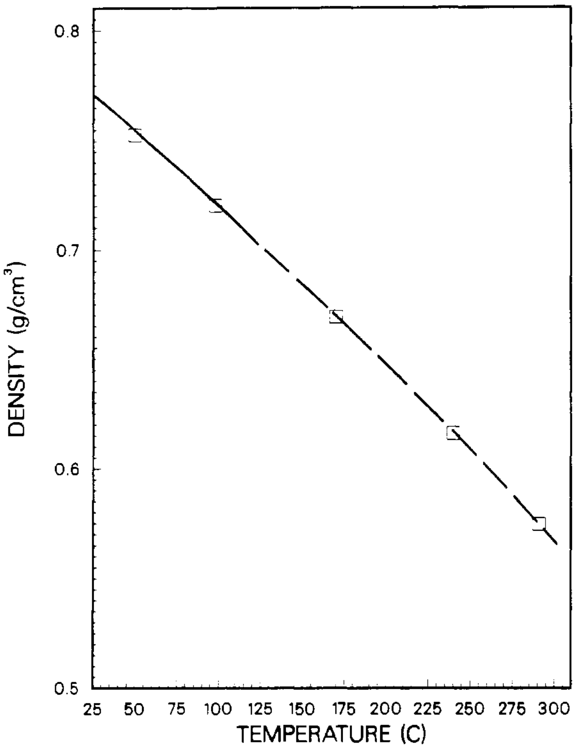

Figure 3. Density of *n*-hexadecane at 205 psia: □, measured; —, calculated from Orwoll and Flory (1967); – – –, best fit of data.

pressures well above ambient.

Glossary

D_{AB}	diffusivity of solute A in solvent B, m^2/s
L	dispersion tube length
$\dot{m}$	mass flow rate
R	dispersion tube radius
T	absolute temperature, K
$\bar{t}$	first temporal moment (retention time)
V	molar volume of solvent, cm^3/g-mol
V_t	dispersion tube volume
β	coefficient in correlation of eq 5
ρ	solvent density, g/cm^3
σ^2	second temporal moment (variance)
ζ_0	defined by eq 3
η	viscosity, cP

Registry No. *n*-Octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3.

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High-Temperature Diffusion of Hydrogen, Carbon Monoxide, and Carbon Dioxide in Liquid *n*-Heptane, *n*-Dodecane, and *n*-Hexadecane

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Mutual diffusion coefficients at infinite dilution have been measured for hydrogen, carbon monoxide, and carbon dioxide in the solvents *n*-heptane, *n*-dodecane, and *n*-hexadecane. The data cover the temperature range from 25 to 293 °C and pressures of 1415 and 3450 kPa. The Taylor dispersion method was used for diffusion measurements. It was found that the Sovova correlation for diffusion of dissolved gases in liquids failed to predict diffusivities at temperatures above ambient. A free-volume approach to correlation is indicated instead.

Introduction

Diffusion coefficients of hydrogen, carbon monoxide, and carbon dioxide are needed in evaluation of mass transport in high-temperature applications such as hydrogenation, hydrotreating, Fischer–Tropsch synthesis, coal liquefaction, etc. The data in the literature are at temperatures and pressures near ambient, and predictive theories based on these data cannot reliably be extrapolated to the high-temperature range. The objective of this work was to measure diffusion coefficients for these gases at temperatures to 293 °C and pressures to 3450 kPa (500 psia).

Experimental Technique

Mutual diffusion coefficients of the three gases were measured by using the Taylor dispersion method. The present device and working equations have been described previously (*1*). In this method, a narrow pulse of solute (A) diluted in the solvent (B) is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance σ^2 is dependent on the average flow velocity $\bar{u}$ and molecular diffusivity D_{AB}. At the end of the diffusion tube the concentration vs. time data $C(t)$

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