

## Mutual Diffusion Coefficients for Two *n*-Octane Isomers in *n*-Heptane<sup>1</sup>

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A new instrument for the measurement of mutual diffusion coefficients in the liquid phase based on the Taylor dispersion technique has been developed. The instrument design and operation are described. The working region of the instrument has been established using an ideal model for the apparatus. The necessary design considerations and corrections to ensure that the instrument operates in accordance with the theory of the method are discussed. The accuracy of the experimental results is estimated to be  $\pm 1\%$ . Experimental data for *n*-octane and 2,2,4-trimethylpentane at infinite dilution in *n*-heptane are reported. Correlation schemes based on the rough-hard sphere theory have been used to represent the experimental data and their predictive capability examined.

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**KEY WORDS:** diffusion coefficient; *n*-heptane; hydrocarbons; *n*-octane; 2,2,4-trimethylpentane.

### 1. INTRODUCTION

Taylor [1] has shown that the dispersion of a pulse of a solute in a fully developed laminar flow of solvent in a circular cross-section tube is the result of the combined action of convection along the axis of the column and molecular diffusion in the radial direction. The coupling of these two effects results in a significant dispersion of an initially concentrated pulse in a relatively short time. Furthermore, the flow of the fluid

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permits a single fixed concentration monitor to observe all of the dispersed solute as a function of elapsed time. The technique therefore provides a rapid and simple means of determining fluid diffusion coefficients. A detailed investigation of the theory of the Taylor dispersion technique for liquid diffusivity measurements has been presented [2]. The theory provides a set of working equations and conditions for an apparatus based on this principle. Taking into account the minor corrections, the systematic errors can be limited to no more than  $\pm 1\%$ . The present paper describes a new instrument based upon the Taylor dispersion technique and its application to the measurement of the diffusion coefficients of mixtures of *n*-heptane with *n*-octane and of *n*-heptane with 2,2,4-trimethylpentane. The rough hard-sphere theory (RHS), which has been used successfully for the interpretation of self-diffusion and mutual diffusion coefficient [3–5], has been used for the correlation and interpretation of the experimental data.

## 2. TAYLOR DISPERSION METHOD

The ideal model of an instrument for the measurement of diffusion coefficients by the technique of Taylor dispersion method consists of an infinitely long straight tube of uniform, circular cross section, radius  $a_0$ , through which a fluid with composition-independent physical properties passes in laminar flow with the mean velocity  $u_0$ . Following the injection of a  $\delta$  function of another fluid of a different composition at a particular axial location in the tube, the combined action of the parabolic velocity profile and molecular diffusion causes dispersion of the injected material. Under suitable conditions, the measurements of the first two temporal moments of the distribution of the concentration perturbation a distance  $L$  downstream from the point of injection allows the mutual diffusion coefficients of the binary fluid mixture,  $D_{12}$ , to be determined according to the equation [2]

$$D_{12} = \frac{A_0}{24\pi\bar{t}_{id}} \left( \frac{\langle 1 + 4\sigma_{id}^2/\bar{t}_{id}^2 \rangle^{1/2} + 3}{\langle 1 + 4\sigma_{id}^2/\bar{t}_{id}^2 \rangle^{1/2} + 2\sigma_{id}^2/\bar{t}_{id}^2 - 1} \right) \left\{ \frac{1}{2} + \frac{1}{2}(1 - \delta_a)^{1/2} \right\} \quad (1)$$

Here  $A_0 = \pi a_0^2$  is the cross-sectional area of the tube.  $\bar{t}_{id}$  denotes the first raw moment of the distribution, and  $\sigma_{id}^2$  its second central moment. In addition,

$$\delta_a = 12.7997\zeta_0 \quad (2)$$

with

$$\zeta_0 = \frac{\bar{u}_0 a_0^2}{48LD_{12}} \quad (3)$$

The design criteria and the small corrections given in Ref. 2 have been taken into account in the construction and operation of the present instrument. Most of the corrections are very small, contributing less than 0.1% to the measured diffusion coefficient. However, the correction to be applied for the extra dispersion occurring in the tube connecting the diffusion tube to the detector is somewhat larger than in some other instruments [6], owing to the detector design, and amounts to 0.5%. Nevertheless, because this correction can be evaluated with an uncertainty of no more than  $\pm 10\%$  [2], the final contribution to the error in the diffusion coefficients is less than  $\pm 0.05\%$ . The corrections that need to be applied amount to no more than 0.7% in any case and are readily estimated.

### 3. INSTRUMENT DESIGN AND OPERATION

The application of the theory of the Taylor dispersion technique [2] leads to the design parameters of the instrument listed in Table I. Figure 1 shows schematically the experimental setup. The detector used was a differential refractometer (Model R410, Waters Associates) which has an internal heat exchanger capable of maintaining the detector cell at a constant temperature to within  $\pm 0.1^\circ\text{C}$ . The quantities  $V_D$  and  $l_c$  are characteristics of the detector required in applying some of the corrections [2]. The diffusion tube was made of stainless steel (1-mm i.d.), wound around a stainless-steel circular ring. The circular ring was suspended using stainless-steel rods inside an oil bath. The bath temperature was maintained to within  $0.1^\circ\text{C}$  using a combined Braun Thermomix 1442D/Frigomix S immersion and circulation thermostat. The sample was injected using a six-port Rheodyne 7010 injection valve equipped with a 7012 loop-filler port and a 10- $\mu\text{l}$  loop. The injector assembly was immersed inside the thermostat oil bath. An HPLC Technology RR/066 pulseless pump was used to deliver the flow of the liquid. A Hewlett-Packard 3390A reporting integrator was used for peak detection and integration. The

Table I. The Characteristics of the Diffusion Apparatus

Diffusion tube length, $L$	$12.236 \pm 0.004$ m
Diffusion tube cross-sectional area, $A_0$	$0.950 \pm 0.002$ mm <sup>2</sup>
Coil radius, $R_c$	$116.0 \pm 0.1$ mm
Injection volume, $V_i$	10 $\mu\text{l}$
Detector volume, $V_D$	10 $\mu\text{l}$
Length of connecting tubing, $l_c$	1.53 m
Radius of connecting tubing	0.11 mm

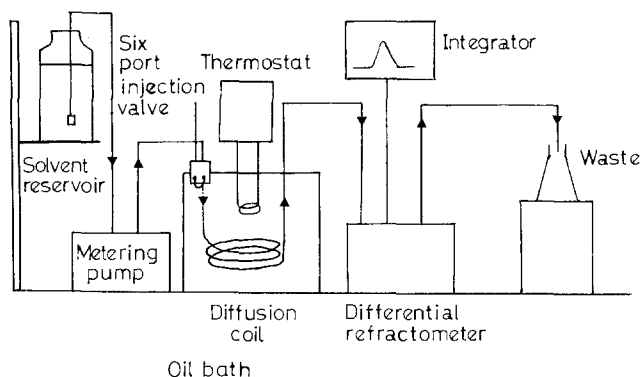


Fig. 1. Schematic diagram of the instrument.

integrator reports the retention time and the peak area/height ( $A/H$ ). The peak width at half-height ( $W_{1/2}$ ) is related to  $A/H$  by

$$W_{1/2} = 0.939437 A/H \quad (4)$$

The first moments of the Gaussian peaks can be determined from the retention time and the second moment from the peak width at half-height ( $W_{1/2}$ ) using

$$W_{1/2} = 2(2 \ln 2)^{1/2} \sigma \quad (5)$$

This method of evaluation of the peak characteristics was compared with the method of regression employed elsewhere [6] and was found to yield consistent second moments within  $\pm 0.1\%$ . In view of this the simpler integrator method was employed routinely for the determination of the data reported here.

#### 4. EXPERIMENTAL

Measurements of mutual coefficients were carried out on the systems *n*-octane in *n*-heptane and 2,2,4-trimethylpentane in *n*-heptane at 35, 40, 45, and 50°C. *N*-Heptane and 2,2,4-trimethylpentane were supplied by J. T. Baker and had purities of 99.9 and 100%, respectively. *N*-Octane was obtained from Aldrich and the purity was  $\geq 99\%$ . The liquids were further purified by distillation and the purity was confirmed using a gas chromatograph. The liquids were filtered using Millipore filters (0.45  $\mu\text{m}$ ) and degassed in an ultrasonic tank followed by helium sparging.

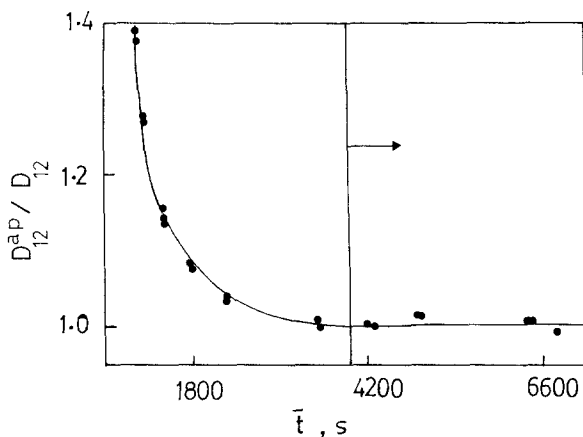


Fig. 2. The experimental determination of the working region of the instrument. (●) Experimental; (→) working region of the instrument.

To ensure that the instrument operates in accordance with theory, the working region of the instrument was established experimentally. This is accomplished by performing diffusion coefficient measurements at a number of different linear velocities. Only if all the conditions of the theoretical treatment are satisfied will the observed diffusion coefficient be independent of the velocity employed [2]. Figure 2 shows the results obtained in several experiments for mutual diffusion of 2,2,4-trimethylpentane in *n*-heptane, with dispersion times between 1000 and 7200 s. It shows that  $D_{12}^{ap}/D_{12}$  sharply decreases with diffusion time and approaches a constant value ( $\pm 1\%$ ). For the measurements reported here, times of  $>4000$  s were used.

## 5. RESULTS

Tables II and III list the results obtained for the mutual diffusion coefficients of *n*-octane and 2,2,4-trimethylpentane at infinite dilution in

Table II. Mutual Diffusion Coefficients for *n*-Octane in *n*-Heptane

Temperature, $T$ (K)	$D_{12}$ ( $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ )
308.15	3.086
313.15	3.366
318.15	3.580
323.15	3.743

**Table III.** Mutual Diffusion Coefficients for 2,2,4-Trimethylpentane in *n*-Heptane

Temperature, $T$ (K)	$D_{12}$ ( $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ )
308.15	2.866
313.15	3.088
318.15	3.253
323.15	3.454

*n*-heptane. For the system *n*-octane/*n*-heptane, the following correlating equation was obtained:

$$D_{12}(T) = 4.918 \times 10^{-11}(T - 273.15) + 1.361 \times 10^{-9} \quad (6)$$

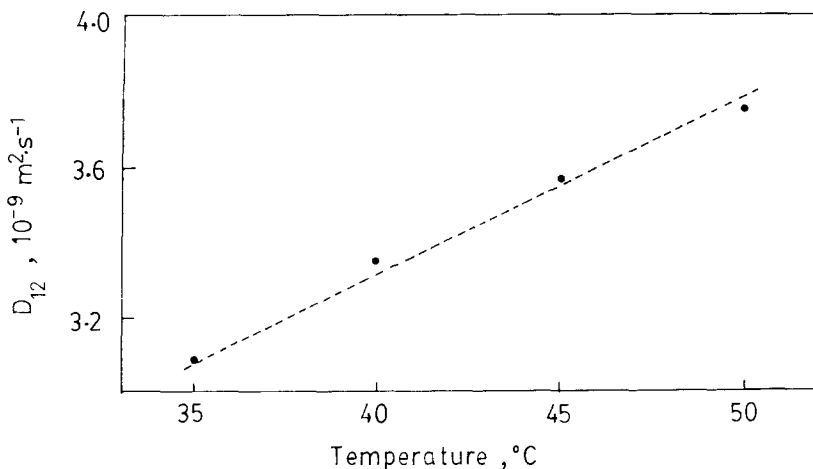
Similarly, for the system 2,2,4-trimethylpentane/*n*-heptane, the following correlating equation was obtained:

$$D_{12}(T) = 3.990 \times 10^{-11}(T - 273.15) + 1.453 \times 10^{-9} \quad (7)$$

where  $D_{12}(T)$  is in  $\text{m}^2 \cdot \text{s}^{-1}$ , and  $T$  is in K.

## 6. DISCUSSION

In Fig. 3 the results reported here for the mutual diffusion coefficient of *n*-octane at infinite dilution in *n*-heptane are compared with a correla-



**Fig. 3.** Mutual diffusion coefficients for *n*-octane in *n*-heptane. (●) Present work; (---) experimental correlation obtained by the same method [6].

tion of the same type determined by the same method [6]. An agreement of better than  $\pm 1\%$  is revealed which is within the mutual uncertainty of the two sets of measurements.

The rough hard-sphere (RHS) model [3, 7, 8] has been applied successfully to the description of the diffusion coefficient of pure liquids. The theory was extended to binary mixtures by Czworniak et al. [9] and Bertucci and Flygare [10]. Based on computer simulation results for the hard sphere, Dymond [3] derived free-volume expressions for the interpretation and correlation of transport property data of dense fluids. For mutual diffusion coefficients at infinite dilution, Chen et al. [11] adopted the following form of the free-volume expression:

$$\frac{D_{12}}{\sqrt{T}} = \beta(V - V'_0) \quad (8)$$

where  $V$  is the molar volume of the solvent. It has been shown [11] that if the rough hard-spheres model applies, a plot of  $D_{12}/\sqrt{T}$  vs molar volume should give a straight line, from which the constants  $\beta$  and  $V'_0$  can be determined. As shown in Fig. 4 there is indeed a linear relationship between  $D_{12}/\sqrt{T}$  vs  $V$  for *n*-octane and 2,2,4-trimethylpentane. Values of the  $\beta$  and  $V'_0$  deduced from Fig. 4 are given in Table IV. Among the two alkanes studied, the intercept  $V'_0$  determined from the regression analysis differs by no more than  $\pm 0.6\%$ .

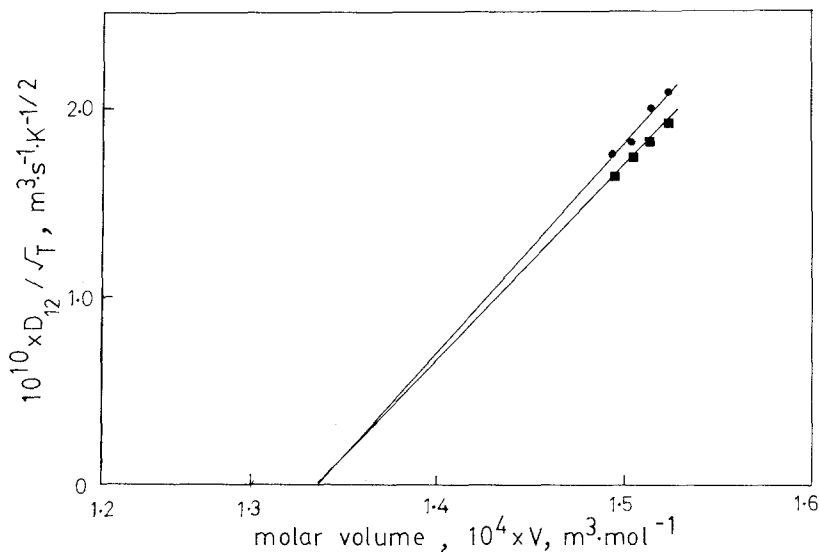


Fig. 4. Plot of  $D_{12}/\sqrt{T}$  vs  $V$  for *n*-octane and 2,2,4-trimethylpentane in *n*-heptane according to Eq. (8). (●) *n*-Octane; (■) 2,2,4-trimethylpentane.

**Table IV.** Coefficients for Eq. (8) for the *n*-Octane/*n*-Heptane and 2,2,4-Trimethylpentane/*n*-Heptane Systems

Solute	$10^5 \beta$ (mol <sup>-1</sup> · m <sup>-1</sup> · s <sup>-1</sup> · K <sup>-1/2</sup> )	$10^4 V'_0$ (m <sup>3</sup> · mol <sup>-1</sup> )
<i>n</i> -Octane	1.113	1.1335
2,2,4-Trimethylpentane	0.974	1.326

Using the values of  $V'_0$  obtained it is possible to calculate the hard-sphere diameter of the solvent because [12]

$$V'_0 = bV_0 = bN\sigma_2^3/\sqrt{2} \quad (9)$$

where  $N$  is Avogadro's constant. Here,  $\sigma_2$  is the hard-sphere diameter of the solvent. The constant  $b$  for self-diffusion has been found to be 1.3509 from linear regression of the data of Eastal et al. [13]. Using  $b = 1.3509$  and the average  $V'_0$  for the two alkane solutes gives  $\sigma_2 = 0.614$  nm for *n*-heptane.

According to Dymond [14] a plot of  $T^{1/2}/\eta$  against the molar volume  $V$  can be used to determine the hard-sphere diameter of a fluid because the intercept at zero fluidity ( $1/\eta$ ) occurs at  $V = 1.384 V_0$ . More recently, molecular dynamics simulations for hard spheres [13] have confirmed this idea, although the intercept has been found to occur at  $V = 1.3509 V_0$ . Using the latter result in conjunction with viscosity data for *n*-heptane at atmospheric pressure in the temperature range 293–353 K, we have obtained a hard-sphere diameter of  $\sigma_2 = 0.614$  nm, which is in complete agreement with the value determined from the present diffusion data.

The following empirical equations obtained for mutual diffusion coefficients at infinite dilution in *n*-alkanes [12] have been suggested for the prediction of the values of  $V'_0$  and  $\beta$ :

$$V'_0 = 0.308 V_c \quad (10)$$

$$\beta = 2.7985 \times 10^{-10} M_A^{-0.61} V'_0{}^{-1.04} \quad (11)$$

Here  $V_c$  is the critical molar volume of the solvent and  $M_A$  is the molecular weight of the solute. The advantage of this approach is that a knowledge of only the solvent critical volume  $V_c$  and the solute molecular weight  $M_A$  is sufficient to allow the parameters  $\beta$  and  $V'_0$  to be determined. It is then possible to calculate the diffusion coefficient of alkanes in dilute concentrations using Eq. (8). The value of  $V'_0$  calculated using Eq. (10) agrees with those determined from the slope of the  $D_{12}/\sqrt{T}$  vs  $V$  plot for the two



alkanes to within  $\pm 0.5\%$ . For *n*-octane the value of  $\beta$  calculated using Eq. (11) agrees with the experimental value to within 1%. However, for 2,2,4-trimethylpentane the experimental value differs from that calculated by about 13%. This is not unexpected since Eq. (11) was derived based on experimental data for *n*-alkanes only. At present, there is insufficient data for formulating reliable correlating equations for branched alkanes. We hope to report additional experimental data and correlating equations for these systems in the near-future.

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