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Mutual Diffusion Coefficients for Binary Mixtures of Normal Alkanes

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This paper describes the design and operation of a new instrument for the measurement of diffusion coefficients in liquid mixtures. The instrument employs the principle of Taylor dispersion and has been designed so that it operates as nearly as possible in accordance with the simplest possible mathematical description of the measurement process. The remaining departures from the simple description are accommodated by means of small corrections which have been evaluated from a detailed theory of a practical instrument so that accurate measurement of diffusion coefficients may be performed. The apparatus has been employed to make a series of measurements of the mutual diffusion coefficient of binary mixtures among the normal alkanes hexane, heptane, and octane. The measurements have been performed at atmospheric pressure in the temperature range 290–340 K and over the entire range of mixture composition. It is estimated that the experimental data have an associated uncertainty of ± 1%. The temperature and composition dependences of the mutual diffusion coefficient have been found to be linear, and the entire body of experimental data is represented by a simple correlating equation within its estimated uncertainty.

KEY WORDS: diffusion coefficient; hydrocarbons; liquid mixtures; Taylor dispersion.

1. INTRODUCTION

The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures have usually been performed by interferometric methods [1, 2]. However, it has proved exceedingly difficult to apply these techniques to conditions far removed from ambient. Consequently, in order to provide experimental data over a wider range of thermodynamic states,

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other techniques have been refined to the stage where they are capable of yielding results with an accuracy only slightly inferior to the best previously attainable [3]. One such method is based upon the phenomenon of Taylor dispersion [4, 5], and a complete theory of an instrument operating upon this principle has recently been given [6]. The method is direct and offers the advantages of speed and simplicity which, together with the availability of a suitable theory and an accurate working equation, makes it possible to design instruments for measurements of diffusion coefficients over a wide range of conditions.

In this paper the theory of the Taylor dispersion method is employed to establish the optimum design of an instrument for the measurement of the mutual diffusion coefficients of binary liquid mixtures at atmospheric pressure in the temperature range 290–400 K. The instrument constructed according to these principles is described and is shown to operate in accordance with the mathematical description of it. The results of a series of measurements of the mutual diffusion coefficients of binary mixtures of *n*-hexane, *n*-heptane, and *n*-octane over the entire composition range and in the temperature range 23–70°C are presented, which have an estimated accuracy of ± 1%.

2. INSTRUMENT DESIGN

2.1. Theory

The ideal model of an instrument for the measurement of diffusion coefficients by the technique of Taylor dispersion consists of an infinitely long straight tube of uniform, circular cross-section, radius a_0, through which a fluid mixture with composition independent physical properties passes in laminar flow with the mean velocity $\bar{u}_0$ [6]. Following the introduction of a δ-function pulse of a mixture 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. The analysis of the dispersion process [6] indicates that, under appropriate conditions, the measurement of the first two temporal moments of the distribution of the concentration perturbation a distance L downstream from the point of injection is sufficient to determine the mutual diffusion coefficient of the binary fluid mixture, D_{12}, according to the equation

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

Here, $A_0 = \pi a_0^2$, in the cross-sectional area of the tube, $\bar{t}_{id}$ denotes the first raw moment of the distribution, and σ_{id}^2 its second central moment. In addition [6],

$$\delta_a = 12.7997\zeta_0 \tag{2}$$

with

$$\zeta_0 = \bar{u}_0 a_0^2/48LD_{12} \tag{3}$$

Equation (1) has been derived subject to a number of conditions which must be satisfied by any experimental arrangement. First, in order to ensure laminar flow,

$$2\bar{u}_0 a_0 \rho/\eta \leqslant 2000 \tag{4}$$

where ρ is the fluid density and η its viscosity. Secondly, the contribution of short term transients to the dispersion process has been neglected in Eq. (1). It has been shown that the consequent error in the working equation amounts to less than ±0.01% provided that [6]

$$\bar{t} > 10a_0^2/D_{12} \tag{5}$$

Finally, the truncation error arising from the series development of the working equation amounts to no more than ±0.01% provided that [6]

$$\bar{t} < 700La_0/D_{12} \tag{6}$$

Any practical instrument for the implementation of this measurement technique must inevitably depart from the ideal model of it in several respects. It is usually necessary to construct the diffusion tube in the form of a helical coil in order to permit its containment in a thermostatic enclosure. For this reason the dimensions of the diffusion tube as well as of the coil must be chosen so as to render the effects of secondary flows negligible. A condition which ensures that such effects contribute no more than 0.05% may be written in the form [6]

$$\bar{t} > \left(\frac{a_0^3L^2\rho}{5\eta D_{12}R_c}\right)^{1/2} \tag{7}$$

where R_c denotes the radius of the helical coil.

Conditions (4)–(6) must be satisfied if the effects to which they relate are to be neglected entirely in the analysis of experimental data in a practical instrument. There is a second group of effects arising from the practical implementation of the measurement scheme which cannot be rendered negligible by design. Nevertheless, account may be taken of these effects by means of small, additive corrections to be applied to the observed moments of the eluted distribution to recover the moments of the ideal experiment. The corrections are therefore to be applied in the form [6]

$$\bar{t}_{id} = \bar{t} + \sum_i \delta\bar{t}_i \tag{8}$$

and

$$\sigma_{id}^2 = \sigma^2 + \sum_i \delta\sigma_i^2 \tag{9}$$

where $\bar{t}$ and σ^2 denote the experimentally determined first raw moment and second central moment, respectively. Analytic expressions have been derived [6] for all the corrections $\delta\bar{t}_i$ and $\delta\sigma_i^2$ which arise in a practical instrument from the use of concentration monitors of nonzero volume, injection pulses of nonzero volume, and from connections between the diffusion tube and the detector. The purpose of the instrument design is then to employ these results to ensure that all of these corrections are small ($< 1\%$) so that they may be estimated with sufficient accuracy that their application introduces a negligible uncertainty into the final diffusion coefficient.

For the purposes of the design of the diffusion tube itself, the corrections of significance are those arising from the nonzero volume of the detector, which, in the present work, acts as a perfectly mixed volume V_D at the end of the diffusion tube, and the nonzero volume of injection pulse, which takes the form of a square pulse injection of volume V_i. The corresponding corrections to the two moments are, adopting the notation of ref. [6],

$$\delta\bar{t}_3 = \frac{L}{\bar{u}_0}\left\{3\zeta_0 - \frac{V_D}{\pi a_0^2 L}\right\} \tag{10}$$

$$\delta\sigma_3^2 = \left(\frac{L}{\bar{u}_0}\right)^2\left\{13\zeta_0^2 - \left(\frac{V_D}{\pi a_0^2 L}\right)^2 - 2\zeta_0\left(\frac{V_D}{\pi a_0^2 L}\right)\right\} \tag{11}$$

$$\delta\bar{t}_4 = -\left(\frac{L}{\bar{u}_0}\right)\left(\frac{V_i}{2\pi a_0^2 L}\right) \tag{12}$$

and

$$\delta\sigma_4^2 = -\frac{1}{12}\left(\frac{L}{\bar{u}_0}\right)^2\left(\frac{V_i}{\pi a_0^2 L}\right)^2 \tag{13}$$

To a good approximation $\bar{t}_{id} = (L/\bar{u}_0)$ and $\sigma_{id}^2 = 2(L/\bar{u}_0)^2\zeta_0$ [6]. If it is required that the corrections to the moments should not exceed ± 1%, then these conditions may be expressed as relationships between the diffusion time $\bar{t}$ and the tube dimensions. For example, the condition for the first moment, which is generally the stronger, requires that

$$\bar{t} > \frac{a_0^2}{48 D_{12}}\left[0.01 + \left(V_D/\pi a_0^2 L\right) + \left(V_i/\pi a_0^2 L\right)\right] \tag{14}$$

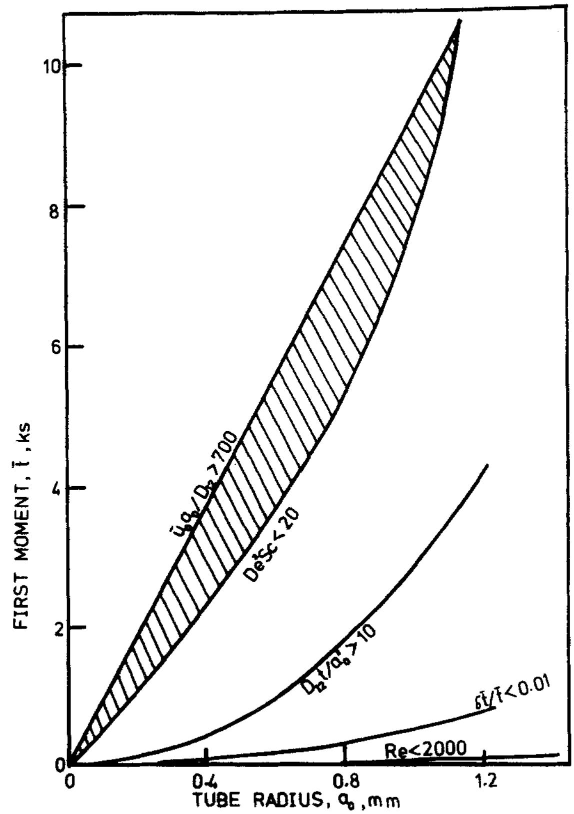

Fig. 1. The operating range for an instrument for the measurement of a diffusion coefficient of 3×10^{-9} $m^2 \cdot s^{-1}$ in a tube of length 15 m and coil radius 0.15 m.

Conditions (4)–(7) and (14) thus provide the criteria for an optimum choice of the dimensions of the diffusion tube and the operating conditions. As an example of the application of these conditions, Fig. 1 contains a plot of the boundaries of the working region for a tube of length $L = 15$ m and coil radius $R_c = 0.15$ m for diffusion coefficient $D_{12} = 3 \times 10^{-9}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$, which is typical of those encountered in the liquid phase. The volume of the detector, V_D, and of the injection pulse, V_i, have both been taken as 10 μl. The region in which all the conditions prescribed above are satisfied is indicated by the hatched area. It can be seen that the region is bounded at long diffusion times by the truncation condition (5) and at short diffusion times by the condition resulting from the effects of secondary flow (7). Thus in order to carry out accurate measurements of the diffusion coefficient prescribed in a tube of the specified length and coil radius, the tube radius and flow velocity must be carefully chosen to be within the hatched region. Similar design curves may be obtained for different tube lengths, L, coil radii, R_c, diffusion coefficients, D_{12}, and the volumes V_D and V_i. An examination of a series of these curves then leads to a choice of the diffusion tube dimensions which satisfies all of the necessary conditions for accurate measurements over the range of diffusion coefficients likely to be encountered in practice. Evidently, such a selection must also include consideration of the availability of suitable tubing and the practicality of the final design.

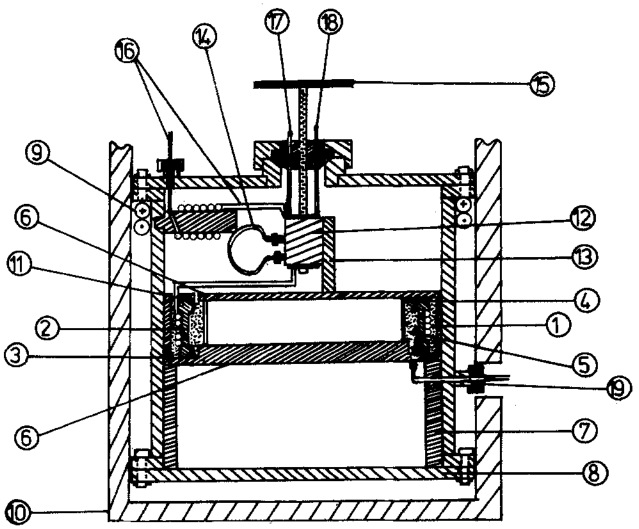

Fig. 2. A vertical section of the thermostatic enclosure containing the diffusion tube.

2.2. The Apparatus

The present instrument has been designed for the measurement of diffusion coefficients in the range 7×10^{-10} to $7 \times 10^{-9}\ m^2 \cdot s^{-1}$ according to the principles outlined in the previous section. Figure 2 contains a vertical section of the thermostatic enclosure which contains the diffusion tube, whereas Fig. 3 displays a flow diagram of the apparatus. The diffusion tube, *1* (Fig. 2), is made from approximately 13 m of 316 stainless steel tubing having a nominal internal diameter of 0.8 mm. The tubing is wound in a smooth helical coil on a ring of copper pillars, *2*, which are supported within the annulus between two copper cylinders *3* and *4*. The annular space is filled with lead, *5*, to increase the heat capacity of the system and thereby damp out temperature fluctuations. The annulus is closed by two copper flanges, *6*, and is supported on three copper pillars, *7*, from the base of the isothermal enclosure, *8*. The latter is itself made of copper and carries heating coils, *9*, on its outer surface through which a suitable heat transfer fluid is pumped from a constant temperature bath. Finally the outer surface of the assembly is surrounded by a layer of insulation, *10*. The temperature of the diffusion tube is measured by means of four thermocouples inserted into ports, *11*, distributed within the lead encasing the tube. It was found that the arrangement maintained the

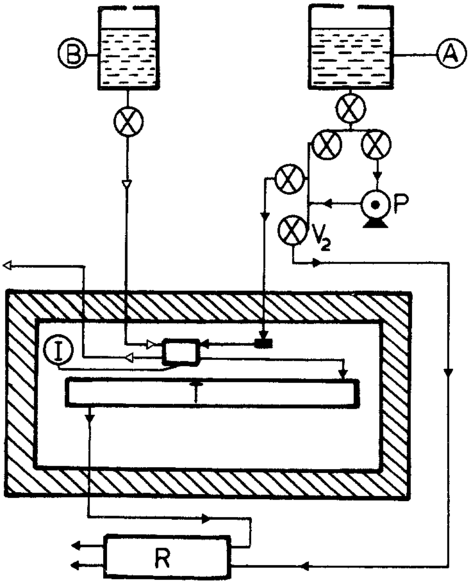

Fig. 3. A flow diagram of the diffusion apparatus.

temperature of the diffusion tube constant and uniform to within ±0.05 K over a period of several hours.

At its upstream end the diffusion tube is directly connected to a six-port, rotary liquid chromatograph injection valve, *12* (Specac Ltd.). The valve is maintained in good thermal contact with the diffusion tube through a metal bracket, *13*, and is equipped with a thermocouple to ascertain that the two elements are at the same temperature. The injection valve is fitted with a sample loop, *14*, of nominal volume 10 μl, and was specially modified to operate at the low internal pressures involved in the present work [7]. The valve may be operated manually from outside of the isothermal enclosure by means of the extension handle, *15*. The carrier fluid is fed to the injection valve by the tube, *16*, which passes through the lid of the isothermal enclosure and is wound around a thermally massive rod inside the enclosure, which acts as a preheater. The sample loop is supplied with material through a tube, *17*, whereas the effluent from the sample loop is taken out through another tube, *18*. At its downstream end the diffusion tube passes through the wall of the isothermal enclosure through the seal, *19*. It is then coupled to one side of a differential refractometer (Waters Associates Inc.) by means of a short length $l_c = 0.35$ m of connecting tubing with an internal diameter of 0.2 mm.

The flow diagram contained in Fig. 3 illustrates schematically the external connections made to the diffusion tube and the sample injection valve. The carrier fluid flow is maintained by the hydrostatic pressure provided by a reservoir of the fluid, A, whose level may be adjusted to secure the desired liquid flow rate. The fluid in the reservoir is continually stirred to ensure a uniform composition at the inlet to the diffusion tube, T, and is isolated from any contamination from the atmosphere. A similar arrangement is employed for the supply of the material for injection from the reservoir, B. The carrier fluid is also used to fill the reference side of the differential refractometer cell R through the valve V_2, which is closed during measurement. Finally, a pump P is included in the liquid lines to permit rapid purging of the system following a change of the working fluid. The reservoir for the carrier fluid was designed in such a way that the change in hydrostatic pressure during the course of a single measurement amounted to no more than 0.1% of the total head. The same figure therefore represents the constancy of the linear velocity of the carrier fluid, which was confirmed by direct measurement of the mass flow rate.

The precise dimensions of the diffusion tube and its ancillary components are listed in Table I. The length of the diffusion tube and the radius of the coil have been determined by direct measurement. However, the treatment of nonuniformities in the bore of the diffusion tube and any ellipticity of the cross-section [6] demonstrates that the effective cross-

Table I. The Characteristics of the Diffusion Apparatus

Diffusion tube length, L	13.219 ± 0.004 m
Diffusion tube cross-sectional area, A_0	$0.527_8 \pm 0.002$ mm^2
Coil radius, R_c	131.8 ± 0.1 mm
Injection volume, V_i	10 mm^3
Detector volume, V_D	10 mm^3
Length of connecting tubing, l_c	0.35 m
Radius of connecting tube, a_c	0.1 mm

sectional area, A_0, is best derived from the volume of the tube and its length because any such effects are then automatically compensated to a high degree of accuracy. In order to permit such an evaluation the volume of the tube has been determined by measuring the mass of water it contains under prescribed conditions.

The differential refractometer employed for the detection of the eluted distribution has an ultimate detection limit of 1×10^{-9} units of refractive index as well as a large range over which the analogue output signal is proportional to the refractive index difference between the sample and the reference sides of the cell. In the present application the output signal of the refractometer is digitized and recorded at preset time intervals, typically every second, on a magnetic tape for subsequent analysis. In order to confirm that the entire detection system produces a linear response to the concentration difference between the fluid in the sample and reference sides of the cell for the liquids studied in the present work, a series of independent measurements has been conducted. The zeroth moment of the eluted distribution in response to injections of mixtures containing progressively greater known concentrations of one component have been determined by direct numerical integration of the recorded distribution. It has been found that the departures from linearity do not exceed $\pm 0.1\%$ until the mole fraction of the injected sample differs by as much as 0.8 from that of the flowing stream. During the diffusion coefficient measurements the mole fraction difference between the injected sample and that of the flowing stream was maintained below ± 0.1 so that linearity of the detection system was assured.

2.3. Data Analysis

The data recorded during a single measurement represent the distribution of the perturbation of the concentration of the flowing stream at the end of the diffusion tube as a function of time. In order to apply the working equation (1) to determine the corresponding diffusion coefficient, it is necessary to evaluate the first two moments of the distribution and then to correct them according to Eqs. (8) and (9). The moments of the distribution may, in principle, be determined by the direct numerical integration of the concentrations, $C(t_i)$, recorded at discrete times, t_i. Normally about 1000 such data points are included in the sample. However, this procedure has not proved as precise as an alternative method based upon the results of the theory of the method [6]. It has been shown [6] that for the conditions employed in the measurements, the eluted concentration distribution should depart negligibly from a gaussian distribution:

$$C(t) = A \exp\left[-(t-\bar{t})^2/2\sigma^2\right] \tag{15}$$

Consequently, the moments $\bar{t}$ and σ^2 may be determined by applying a nonlinear fitting procedure to represent the recorded data by an equation of the form of (15) in which they are treated as parameters. A similar method has been proposed by Andersson and Berglin [8] except that for the conditions of their work it was necessary to include terms of higher order in Eq. (15) to obtain a satisfactory representation of the data.

Figure 4 illustrates the results of our fitting procedure applied to just one measurement in which a solution of *n*-heptane in *n*-hexane with a heptane mole fraction of 0.1 has been injected into pure hexane. Many of

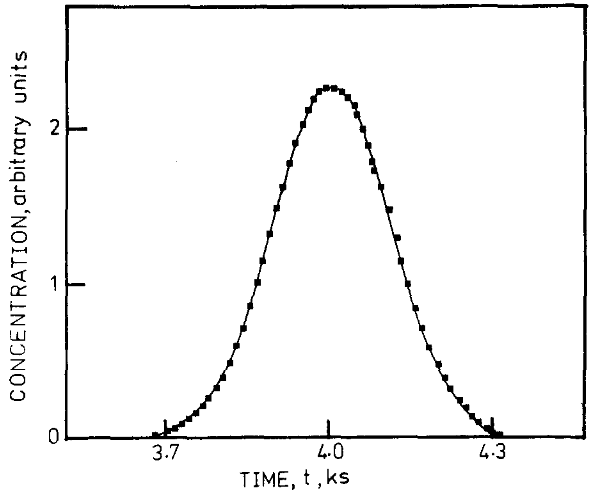

Fig. 4. The eluted distribution for a typical measurement carried out in *n*-heptane/*n*-hexane mixtures. ■, experimental points; ———, the optimum fit of Eq. (15) to the data.

the experimental points have been omitted to preserve clarity, but it can be seen that the simple gaussian form provides a good description of the observed distribution. Generally, the fit to the recorded data was commensurate with the precision of the recorded voltage measurements (±0.1% of the value at half of the peak height). It may be noted here that these results provide confirmation that the instrument operates in accordance with the mathematical description of it.

2.4. Precision and Accuracy

It is difficult to estimate the uncertainty involved in the determination of the moments of the distribution by the method described above. Consequently, we have preferred to employ the reproducibility of the results of a series of experiments under nominally identical conditions as a measure of the precision of the moments. Generally, the first moment is found to be reproducible within ±0.2%, whereas the variance has an uncertainty of ±0.5%.

The only corrections to the observed moments which it has been found necessary to apply in the present work are those which arise from the nonzero volumes of the detector and injection sample and from the small length of connecting tubing between the diffusion tube and the detector [6]. In a typical experiment the total correction to be applied to the first moment is no more than ±0.5%, whereas that for the variance is at most one of ±0.7%. Because those corrections are readily estimated with an uncertainty of less than ±5%, their contribution to the final diffusion coefficient reported amounts to no more than ±0.1%.

A further correction must be applied to the reported results in order to account for the fact that the physical properties of the fluid mixture, in particular, the diffusion coefficient itself, depend upon composition in contrast with the assumptions of the ideal model of the measurement [6, 7]. This correction has been expressed as a change in the mixture composition to which the reported diffusion coefficient refers by means of the equation [7]:

$$x_{\mathrm{ref}} = x_f + \delta x \tag{16}$$

Here, x_f represents the mole fraction of the flowing stream and δx the correction for which an analytic expression has been given elsewhere [6, 7]. Generally the correction δx does not exceed ±0.003 so that the additional uncertainty introduced is negligible. The overall accuracy of the reported diffusion coefficients, including the uncertainty in the cross-sectional area of the diffusion tube, is estimated to be one of ±1%.

3. EXPERIMENTAL

Measurements have been carried out of the mutual diffusion coefficients of binary mixtures among the normal alkanes *n*-hexane, *n*-heptane, and *n*-octane in the temperature range 23–70°C. The measurements have been performed for five different compositions for each of the mixtures. The pure liquids were supplied by BDH Chemicals Ltd. and had a stated purity of better than 99–99.5%. The liquids were further purified by distillation and degassification until chromatographic analysis indicated that the purity was in excess of 99.9%. The binary mixtures were manufactured gravimetrically, and the error in the quoted mole fractions is estimated to be less than 0.0001.

The measurements have been performed upon each liquid mixture over a range of temperatures. For each set of conditions, measurements have been carried out to provide additional evidence that the instrument operates in accordance with its theory. This is most readily 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 [6]. Specifically, such measurements permit the working region to be defined experimentally so that it can be established that effects owing to coiling of the diffusion tube and natural convection have been rendered negligible. Figure 5 contains the results of one such series of

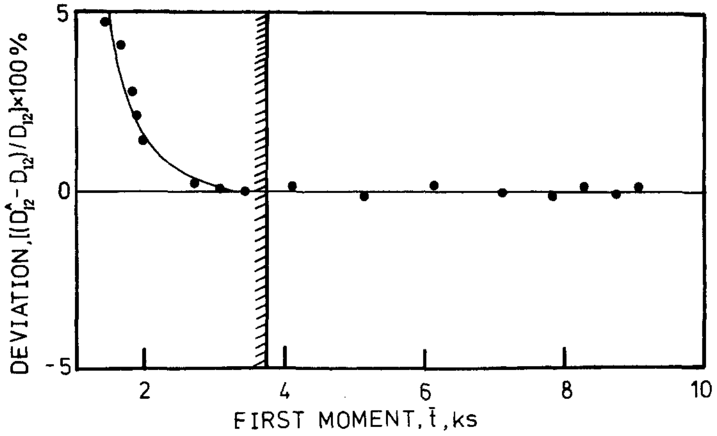

Fig. 5. The experimental determination of the working region of the instrument. The deviations of the apparent diffusion time for the *n*-heptane/*n*-hexane system. ●, experimental data; ———, theoretical prediction [9].

measurements for the *n*-hexane/*n*-heptane system in which the deviations of the apparent diffusion coefficient from the true value are plotted as a fraction of the observed first moment of the distribution. It can be seen that at high linear velocities, the apparent diffusion coefficient departs considerably from the true value because of the mixing effects caused by secondary flow in the coiled tube. The solid line indicates the behavior expected on the basis of the theoretical description of this effect [9], which is in substantial agreement with the experimental observations. The vertical line denotes the limit of the working region defined by the inequality (7) and, within this region, the diffusion coefficient departs from a constant value by no more than ±0.5%. On the basis of this and other similar plots, measurements were normally carried out with diffusion times of between 1 and 2 h, and the diffusion coefficients reported are the mean of several independent determinations.

4. RESULTS

Tables II–IV list the entire body of our experimental results for the mutual diffusion coefficient of the binary systems *n*-hexane/*n*-heptane, *n*-hexane/*n*-octane, and *n*-heptane/*n*-octane, respectively. The data have been corrected to nominal temperatures by the application of small, linear corrections. Figure 6 contains an example of the composition dependence of the diffusion coefficient along isotherms for the *n*-hexane/*n*-octane system. The variation of the diffusion coefficient with *n*-octane mole fraction is linear as was also the case for the other systems. The temperature dependence of the diffusion coefficient has also been found to be

Table II. Mutual Diffusion Coefficients for *n*-Hexane/*n*-Heptane Mixtures

	Heptane mole fraction, x_1				
	0.0016	0.3015	0.4985	0.6985	0.9985
Temperature, T (K)	Diffusion coefficient, $10^9 D_{12}$ ($m^2 \cdot s^{-1}$)				
300	3.72	3.64	3.55	3.53	3.41
308	4.12	4.03	3.97	3.90	3.65
315	4.55	4.38	4.30	4.22	4.17
323	4.86	4.77	4.71	4.65	4.56
328	5.10	5.03	4.91	4.89	4.83
333			5.18	5.10	5.04

Table III. Mutual Diffusion Coefficients for *n*-Hexane/*n*-Octane Mixtures

Temperature, T (K)	Octane mole fraction, x_1: 0.0020	0.2023	0.4987	0.7038	0.9980
	Diffusion coefficients, $10^9 D_{12}$ ($m^2 \cdot s^{-1}$)				
295	3.25	3.04	2.81	2.60	2.34
300	3.48	3.28	3.04	2.85	2.57
308	3.85	3.65	3.40	3.23	2.97
315	4.16	3.99	3.74	3.54	3.30
323	4.57	4.37	4.11	3.90	3.67
328	4.79	4.61	4.37		
333				4.39	4.13

Table IV. Mutual Diffusion Coefficients for *n*-Heptane/*n*-Octane Mixtures

Temperature, T (K)	Octane mole fraction x_1: 0.0030	0.2513	0.4988	0.7488	0.9990
	Diffusion coefficient, $10^9 D_{12}$ ($m^2 \cdot s^{-1}$)				
293	2.59	2.50	2.41	2.32	2.23
308	3.21	3.13	3.05	2.94	2.88
323	3.82	3.74	3.64	3.58	3.46
333	4.24	4.13	4.07	3.98	3.89
343	4.74	4.60	4.53	4.43	4.35

Table V. The Coefficients of the Correlating Equation (17)

System	$10^9 a_0$ ($m^2 \cdot s^{-1}$)	$10^{11} a_1$ ($m^2 \cdot s^{-1} \cdot K^{-1}$)	$10^{10} b$ ($m^2 \cdot s^{-1}$)
n-Hexane/*n*-heptane	2.449	4.85	3.45
n-Hexane/*n*-octane	2.210	4.70	8.83
n-Heptane/*n*-octane	1.744	4.21	3.53

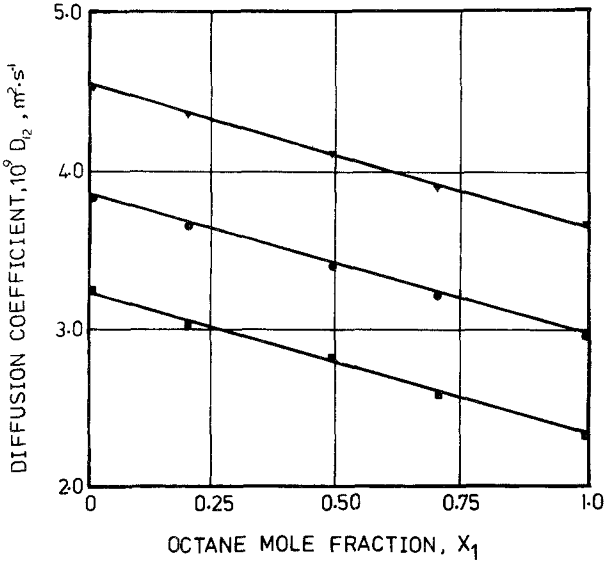

Fig. 6. The isothermal composition dependence of the mutual diffusion coefficient for the *n*-hexane/*n*-octane system. ■, T = 295 K; ●, T = 308 K; ▼, T = 323 K.

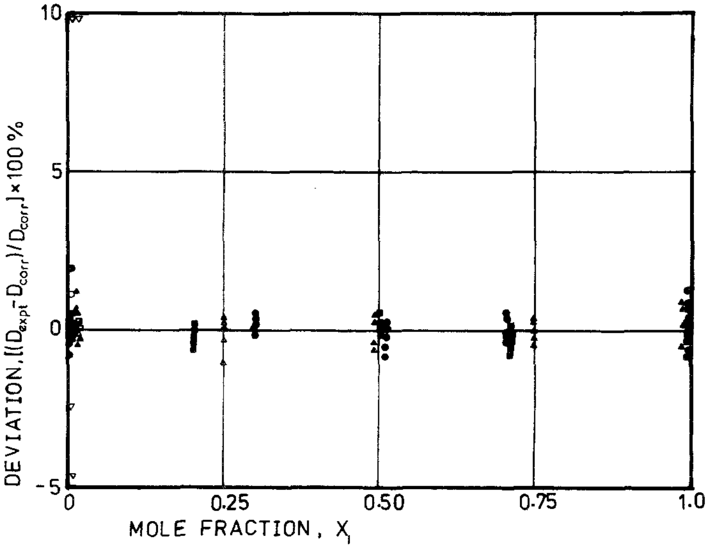

Fig. 7. Deviations of the experimental diffusion coefficients from the correlation of Eq. (17) and Table V. *n*-Hexane/*n*-heptane: ●, present work; ○, [11]; ◐, [12]. *n*-Hexane/*n*-octane: ■, present work; □, [11]; ◪, [12]. *n*-Heptane/*n*-octane: ▲, present work; △, [11]; ▲, [12]; ▽, [13].

linear within the range of temperatures studied in this work. Consequently, it is possible to give a compact representation of the experimental data in the form

$$D_{12}(x_1, T) = a_0 + a_1(T - 273.15) - bx_1 \tag{17}$$

in which x_1 is the mole fraction of the heavier component. The coefficients of this correlation for the three systems are given in Table V, whereas Fig. 7 contains a plot of the deviations of the experimental data from the correlation. The deviations do not exceed ±1.3%, the standard deviation being one of ±0.5%. The same figure includes a comparison with the sparse experimental data previously reported for these systems [10–13]. The deviations of these earlier results from the present correlation amount to as much as 10% in some cases. The present experimental data are to be preferred owing to their higher accuracy.

5. CONCLUSIONS

The instrument described in this paper has been shown to yield diffusion coefficients for liquid mixtures over a modest temperature range with an accuracy of ±1%, which is comparable with that attainable by techniques such as the diaphragm cell [10–12]. This may be taken to be representative of what could be achieved over wider ranges of conditions with careful attention to the design of the instrument. At the same time it should be pointed out that the Taylor dispersion technique employed here offers the advantage of speed compared with many other techniques.

The development of the successful van der Waals model of the dense fluid state to describe the process of binary diffusion in liquid mixtures has recently been carried out by Czworniak et al. [14]. However, there is at present insufficient information available to permit a comparison of the results of this work with the present experimental data. In particular, there are no viscosity data available for the systems studied here which are of sufficient reliability to warrant an analysis of this type at present.

It is worthwhile pointing out, in conclusion, that of the many empirical correlation and prediction schemes for the diffusion coefficients of binary liquid mixtures, the one proposed by Lusis and Ratcliff [15] for the diffusion coefficient at infinite dilution of one component is superior to the others. The deviations of the predictions from the present experimental data do not exceed ±4% for any system. The linear composition dependence of the diffusion coefficient along an isotherm observed in this work is consistent with the findings of several authors [10, 16, 17] for nearly ideal mixtures.

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