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Transport Properties of Nonelectrolyte Liquid Mixtures. XI. Mutual Diffusion Coefficients for Toluene + n-Hexane and Toluene + Acetonitrile at Temperatures from 273 to 348 K and at Pressures up to 25 MPa

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Mutual diffusion coefficients, D_{12}, have been measured at pressures up to 25 MPa using the chromatographic peak broadening technique (Taylor dispersion method) for x toluene + $(1-x)$ n-hexane in the temperature range 298 to 348 K and for x toluene + $(1-x)$ acetonitrile in the temperature range 273 to 348 K. The estimated uncertainty is ±4%. Both systems show negative deviations from straight-line behavior. The fractional decrease in D_{12} is about 0.8% per MPa. Hard-sphere theory is applied under limiting conditions where one of the components is present in a trace amount. It is shown that the diffusion coefficients can be estimated by the Dullien method from a knowledge of the viscosity and density under the same conditions.

KEY WORDS: acetonitrile; Enskog theory; hexane; high pressures; mutual diffusion coefficients; Taylor dispersion; toluene.

1. INTRODUCTION

For a rigorous test of any theory, it is necessary to have experimental measurements for selected systems over a wide range of experimental conditions. In the case of self-diffusion coefficients, accurate measurements have been made on a number of pure nonelectrolyte liquids over a wide range of temperature and pressure by the NMR spin-echo method and radiotracer high-pressure diaphragm cell method, particularly by the

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groups of Lüdemann, Harris and Woolf, and Herz (e.g., Refs. 1–3 and references therein). On the basis of such data, a satisfactory method for correlation has been developed which is based on the hard-sphere model [4, 5]. Limiting intradiffusion measurements in mixtures have been made at pressures up to 400 MPa using a high-pressure diaphragm cell [6], and these data were successfully interpreted on the basis of the rough hard-sphere model.

For mutual diffusion (interdiffusion) in liquid mixtures, most of the experimental work in the past has been restricted to measurements at trace concentration in a limited temperature range and at atmospheric pressure by the Gouy interferometric method and chromatographic peak broadening (Taylor dispersion) method. Measurements above atmospheric pressure have been made using the Taylor dispersion technique by, for example, Akgermann and co-workers up to 3.5 MPa [7, 8]. However, these mutual diffusion values are just at infinite dilution. Here, the hard-sphere model again provides a satisfactory basis for data correlation [8, 9].

The system methane + decane is one of the few for which mutual diffusion data have been measured over the complete composition range at elevated pressures [10]. The method used was Mach–Zehnder interferometry at a temperature of 303 K and a pressure range from 30 to 60 MPa. Over a smaller pressure range, up to a maximum of 25 MPa, a limited number of mutual diffusion coefficient measurements have been made for mixtures by the chromatographic peak broadening method [11–13].

To gain more information on the pressure dependence of the mutual diffusion coefficient over the complete composition range, measurements have been conducted on mixtures of toluene + *n*-hexane over the temperature range 298 to 348 K at toluene mole fractions of 0, 0.25, 0.5, 0.75, and 1.0 up to 25 MPa. Measurements were also made for toluene + acetonitrile mixtures from 273 to 348 K at toluene mole fractions of 0, 0.2, 0.4, 0.6, 0.8, and 1 up to 24 MPa. From these results, the pressure dependence has been calculated for each composition at each temperature.

The approach of Chhabra [14] in relating the pressure dependence of self-diffusion coefficients of simple nonpolar liquids to the viscosity and molar volume is examined with regard to these interdiffusion coefficient data. Finally, the rough hard-sphere theory is applied to the results at infinite dilution to determine the temperature and pressure dependence of the translational–rotational coupling factor.

2. MATERIALS

The *n*-hexane, toluene, and acetonitrile were purchased from Aldrich Chemical Co. Ltd., Gillingham, UK, with stated minimum purities of

99.9 mol%. The measured densities at 298.15 K for toluene, hexane, and acetonitrile were 862.0, 655.0, and 776.7 $\mathrm{kg \cdot m^{-3}}$, respectively, compared with literature values of 862.2 [15], 655.1 [16], and 776.6 [17] $\mathrm{kg \cdot m^{-3}}$. Refractive index measurements were made using a 60/ED Abbe refractometer (Bellingham and Stanley, England). The measured n_D values at 298.15 K were 1.3748 for *n*-hexane, 1.4961 for toluene, and 1.3443 for acetonitrile. The liquids were used as received without further purification but were degassed before use.

3. EXPERIMENTAL

Mutual diffusion coefficients of toluene + *n*-hexane and toluene + acetonitrile mixtures were measured by the Taylor dispersion (peak-broadening) technique [18–20]. An Altex Model 110A metering pump was used to maintain a steady laminar flow of solvent or mixture in a coiled 316 stainless-steel capillary tube of nominal $\frac{1}{16}$-in. outer diameter. Coil A, which had an inner radius of 0.0383 cm and a length of 2040 cm, was mounted on a former of radius 11.36 cm, and coil B, with an inner radius of 0.0406 cm and a length of 2996 cm, was on a former of radius 4.350 cm. The internal radii were determined from measurements of flow rate and mean residence time. Small volumes (10 to 20 $\mathrm{mm^3}$) of solution having a concentration slightly different from that of the carrier solution were introduced into the carrier stream through a liquid chromatography injection valve, Model 7126. The concentration profile of the emerging solution was monitored on an Altex Model 153 UV detector or an LDC Refracto-Monitor Model 1107 and recorded on a variable speed Tekman Electronic recorder.

The theory of the Taylor dispersion technique is well established [18–20]. The ideal model for an apparatus to measure diffusion coefficients by this technique is an infinitely long, straight, and impermeable tube of uniform circular cross section, through which flows an incompressible liquid in the laminar regime. A mixture of the same components but with different composition is injected into the tube as a delta-function pulse that is dispersed by the combined action of molecular flow and the parabolic velocity profile. Provided that certain conditions are satisfied [18, 19], the concentration profile at the end of the diffusion tube results in a Gaussian curve, whose variance σ^2 is related to the diffusion coefficient D_{12} by the equation

$$\sigma^2 = \frac{R_0^2 t}{24 D_{12}} \tag{1}$$

where R_0 is the internal radius of the diffusion tube and t is the retention time of the injected sample in the tube.

In practice, the diffusion tube of several meters in length is usually wound on a former in the form of a coil for isothermal measurements. This gives rise to secondary flow in the curved tube, and the observed diffusivity is higher than the true value. The effect of this secondary flow can be made negligible by suitable choice of conditions [21], by having a sufficiently high retention time. Where this is not possible, corrections for secondary flow can be made following the investigations by Nunge et al. [22], Golay [23], and Tijssen [24]. For an experimental flow rate F, Atwood and Goldstein [11] estimated the diffusion coefficient D_{12}(corrected) that would have been obtained if the tube were straight from the relationship

$$D_{12}(\text{corrected}) = D_{12}(\text{obs})[1 - a(F/F_{\text{Tr}})^4] \tag{2}$$

where D_{12}(obs) is the value of the diffusion coefficient derived from the Gaussian curve with Eq. (1), and a has the value of 0.1034, following Nunge et al. [22], which gives the closest representation to the observed behavior [11]. F_{Tr} is a transition flow rate, defined [25] as the flow rate in a curved tube at which the secondary flow becomes significant compared to diffusion as the process which determines dispersion. It is related to the tube geometry, liquid viscosity η, and density ρ by the equation

$$F_{\text{Tr}} = (518 R r D_{12} \eta / \rho)^{1/2} \tag{3}$$

where r is the internal radius of the diffusion tube and R is the radius of curvature of the coil. As a test of this correction, coil B, with the smaller helical radius, was used to produce a marked secondary flow effect. D_{12} measurements were made at 299.15 K and at atmospheric pressure for toluene diffusing in n-hexane, and for n-hexane in toluene, at flow rates of 0.1, 0.2, 0.4, and 0.5 $\text{cm}^3 \cdot \text{min}^{-1}$. In the former case, the toluene concentration in hexane in the injected sample was 0.1% (v/v) and the UV detector was used; in the latter case, the n-hexane concentration in toluene was 10% (v/v) in the injected sample and the refractomonitor was used. The results are presented in Table I, where the D_{12} values are given, together with their standard deviations. The ratio of the observed diffusion coefficient to the corrected value using Eqs. (2) and (3) is plotted against the normalized flow rate in Fig. 1. The points for the two systems lie on a common curve, showing that this is a characteristic curve for this coil. The predicted curve agrees with the experimental results for a normalized flow rate up to nearly 1, as found previously from measurements with different systems using coils with different characteristics by Atwood and Goldstein [11].

Table I. Observed D_{12} Values for Different Flow Rates at 299.2 K and 0.1 MPa

Flow rate, F ($cm^3 \cdot min^{-1}$)	D_{12}(obs) ($10^9 m^2 \cdot s^{-1}$)	F/F_{Tr}	D_{12}(obs) ($10^9 m^2 \cdot s^{-1}$)	F/F_{Tr}
	Toluene in *n*-hexane		*n*-Hexane in Toluene	
0.1	4.40 ± 0.05	0.380	2.48 ± 0.02	0.427
0.2	4.45 ± 0.05	0.760	2.58 ± 0.05	0.855
0.4	6.08 ± 0.06	1.521	3.81 ± 0.04	1.709
0.5	7.45 ± 0.01	1.901	4.73 ± 0.01	2.137
0.6	8.87 ± 0.12	2.281	5.64 ± 0.02	2.654

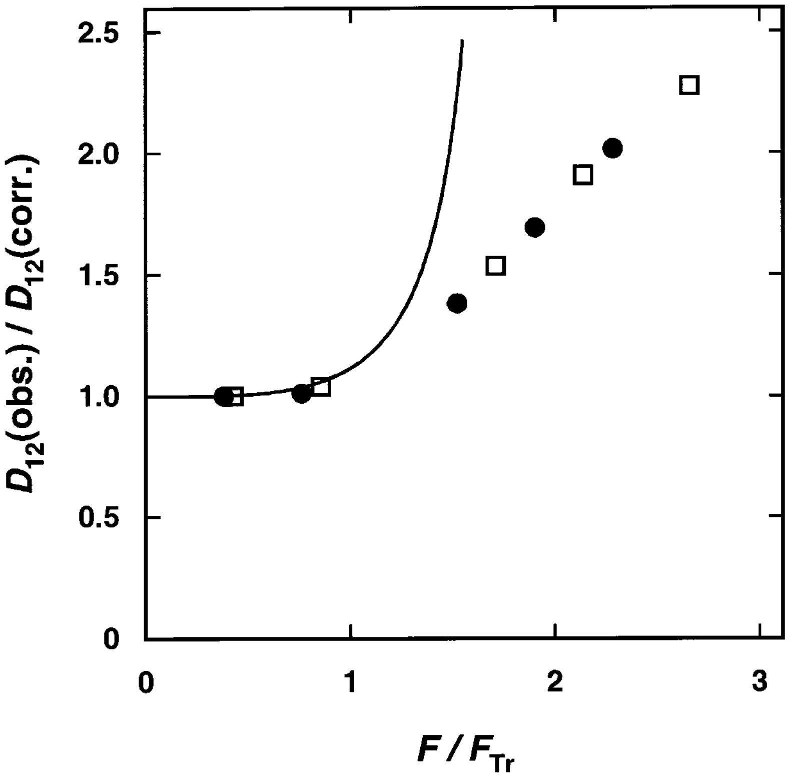

Fig. 1. Ratio of the observed diffusion coefficient ratio, D_{12}(obs), to the value calculated from Eqs. (2) and (3), D_{12}(corr), as a function of the normalized flow rate of the mobile phase. (●) Toluene in *n*-hexane and (□) *n*-hexane in toluene at 299.2 K and 0.1 MPa. Solid line: Eq. (2) with $a = 0.1034$.

To determine the likely error resulting from correction of observed diffusion coefficient values at a normalized flow rate of $0.2\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$, D_{12} measurements were made for *n*-hexane, *n*-decane, and *n*-tetradecane [at concentrations of 5% to 10% (v/v), with the refractomonitor detector] in toluene at 299.2, 323.2, and 348.2 K with coil B at flow rates of 0.1 and $0.2\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$. The results are presented in Table II. The average deviation between the results for a flow rate of $0.2\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$, after correction using Eqs. (2) and (3), and the values obtained at a flow rate of $0.1\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ is less than 2%. The corrected values for *n*-decane in toluene and for *n*-tetradecane in toluene are in excellent agreement with other measurements [26]. For *n*-hexane in toluene, the present results agree closely with the value of Ghai and Dullien [27] at 298.2 K. The results of Chen and Chen [26] for this system are lower, and the 348.2 K value does not lie on a linear $\log D_{12}$ versus $1/T$ plot. In this work, all results for $D_{12}(\mathrm{obs})$ at flow rates higher than $0.1\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ were corrected for secondary flow by application of Eqs. (2) and (3).

High pressure was generated using small pieces of 316 stainless-steel crimped capillary, with an initial internal radius of 0.04 cm. It has been reported [28] that this method raises the mobile phase pressure in the

Table II. Observed and Corrected D_{12} Values for *n*-Hexane, *n*-Decane, and *n*-Tetradecane in Toluene at 0.1 MPa

	$D_{12}\ (10^{-9}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1})$			
T (K)	$F = 0.1\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$	$F = 0.2\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$	Corrected	From Ref. 26
	n-Hexane in toluene			
299.2	2.48 ± 0.02	2.58 ± 0.05	2.48	2.41[a]
323.2	3.30 ± 0.04	3.51 ± 0.03	3.34	3.25
348.2	4.33 ± 0.03	4.57 ± 0.02	4.38	(4.37)[b]
	n-Decane in toluene			
299.2	1.82 ± 0.01	1.99 ± 0.01	1.85	1.87[a]
323.2	2.51 ± 0.02	2.68 ± 0.03	2.44	2.41
348.2	3.20 ± 0.02	3.56 ± 0.04	3.30	3.21
	n-Tetradecane in toluene			
299.2	1.45 ± 0.01	1.65 ± 0.01	1.46	1.45[a]
323.2	1.99 ± 0.01	2.24 ± 0.02	1.93	1.97
348.2	2.60 ± 0.02	3.00 ± 0.02	2.65	2.61

[a] At 300.2 K.

[b] Interpolated from an Arrhenius plot of data from Ref. 26, as the published value at this temperature is obviously incorrect.

diffusion tube without changing the flow rate. In this work, it was found that a slight increase in flow rate resulted at the highest pressures.

Measurements were made with the crimped capillary tubing connected either directly to the diffusion tube or to the outlet side of the UV detector when the high-pressure cell was installed. The close agreement of the mutual diffusion coefficient values ($10^{-9}\,m^2 \cdot s^{-1}$) for toluene in *n*-hexane at 299.2 K and 7.0 MPa of 4.11 and 4.13, respectively, showed that the results were not affected by the position of the tubing. When the refractomonitor was used for detection, the capillary had to be connected before the detector. It was immersed in water at room temperature to avoid baseline drift. Since the residence time in the cooling and pressure reducing section is negligible compared with the period over which dispersion proceeds at room temperature, the perturbation on the measured diffusivities caused by temperature and pressure reduction is expected to be negligible [29]. A 2.8-cm length of crimped capillary tubing was found to raise the pressure to about 6 MPa, while pressures of about 10 and 20 MPa were attained using lengths of 5 and 8 cm of crimped capillary, respectively, at a flow rate of $0.2\,cm^3/min$. The pressure was measured using a Budenberg Gauge Co., Ltd., Broadheath Standard test gauge which can be read to 0.1 MPa. This had been calibrated using a primary standard.

The mixtures were prepared by weight. The less volatile component was weighed first into a small vessel, which was sealed, and then the second component added. The volumes were determined so as to minimize the vapor space to prevent composition changes. The system was brought to the required temperature, and the mobile phase was pumped through the loop. The flow rate was monitored throughout the run as well as during the elution of the peaks using a phase separation flow-rate meter, which had a stated uncertainty of ±1%.

For each mixture, the concentration of the injected solution was adjusted so as to give well-defined peaks. In practice, for the *n*-hexane + toluene system, the injected solutions were richer in *n*-hexane. The effect of change in the concentration of the injected sample on D_{12} for a given

Table III. Effect of Injected Solution Composition on D_{12} Values for Equimolar *n*-Hexane + Toluene at 299.15 K and 0.1 MPa

Composition of injected solution (x hexane)	D_{12} ($10^{-9}\,m^2 \cdot s^{-1}$)
0.546	2.789 ± 0.041
0.592	2.737 ± 0.014
0.688	2.740 ± 0.014
0.788	2.760 ± 0.034

Table IV. Experimental Mutual Diffusion Coefficients for x Toluene + $(1-x)$ Hexane

	x								
	299.15			323.15			348.15		
T (K)	P (MPa)	D_{12} (10^{-9} $m^2 \cdot s^{-1}$)	F ($cm^3 \cdot min^{-1}$)	P (MPa)	D_{12} (10^{-9} $m^2 \cdot s^{-1}$)	F ($cm^3 \cdot min^{-1}$)	P (MPa)	D_{12} (10^{-9} $m^2 \cdot s^{-1}$)	F ($cm^3 \cdot min^{-1}$)
0.00	0.1	4.40 ± 0.04	0.20	0.1	5.59 ± 0.01	0.20	0.1	7.00 ± 0.06	0.30
	10.0	4.01 ± 0.06	0.19	10.0	5.06 ± 0.08	0.20	9.9	6.29 ± 0.04	0.19
	16.8	3.67 ± 0.05	0.31	16.5	4.77 ± 0.03	0.30	16.6	5.88 ± 0.05	0.30
	24.2	3.54 ± 0.02	0.31	24.3	4.54 ± 0.03	0.31	24.2	5.57 ± 0.04	0.31
0.25	0.1	3.35 ± 0.03	0.30	0.1	4.39 ± 0.06	0.19	0.1	5.58 ± 0.03	0.19
	7.5	3.05 ± 0.06	0.30	6.7	4.15 ± 0.05	0.30	6.8	5.22 ± 0.08	0.30
	15.6	2.88 ± 0.06	0.32	15.2	3.89 ± 0.06	0.32	16.6	4.83 ± 0.06	0.32
	22.8	2.78 ± 0.02	0.31	23.7	3.65 ± 0.04	0.32	24.2	4.44 ± 0.08	0.33
0.50	0.1	2.79 ± 0.04	0.20	0.1	3.60 ± 0.03	0.10	0.1	4.57 ± 0.05	0.10
	9.8	2.56 ± 0.03	0.20	9.8	3.45 ± 0.06	0.20	8.6	4.47 ± 0.05	0.20
	16.0	2.47 ± 0.04	0.22	16.5	3.26 ± 0.07	0.21	16.6	4.18 ± 0.07	0.21
	25.4	2.26 ± 0.06	0.35	24.0	3.00 ± 0.04	0.33	23.8	3.98 ± 0.05	0.34
0.75	0.1	2.50 ± 0.04	0.20	0.1	3.28 ± 0.07	0.10	0.1	4.28 ± 0.03	0.20
	8.0	2.38 ± 0.04	0.20	8.2	3.14 ± 0.05	0.20	7.1	4.19 ± 0.08	0.20
	17.8	2.25 ± 0.06	0.22	16.5	3.02 ± 0.04	0.22	15.5	3.92 ± 0.09	0.22
	22.8	2.18 ± 0.03	0.35	23.1	2.87 ± 0.08	0.34	22.8	3.78 ± 0.08	0.34
1.00	0.1	2.52 ± 0.03	0.19	0.1	3.21 ± 0.08	0.20	0.1	4.17 ± 0.07	0.19
	7.5	2.34 ± 0.03	0.20	7.4	3.14 ± 0.02	0.20	7.7	4.01 ± 0.02	0.20
	15.9	2.23 ± 0.02	0.20	15.4	2.99 ± 0.06	0.20	15.0	3.80 ± 0.04	0.20
	24.8	1.98 ± 0.03	0.30	23.8	2.80 ± 0.07	0.30	24.0	3.59 ± 0.03	0.30

Table V. Experimental Mutual Diffusion Coefficients for x Toluene + $(1-x)$ Acetonitrile

	x											
	273.15			298.15			323.15			348.15		
T (K)	P (MPa)	D_{12} (10^{-9} m$^2\cdot$s^{-1})	F (cm$^3\cdot$min^{-1})	P (MPa)	D_{12} (10^{-9} m$^2\cdot$s^{-1})	F (cm$^3\cdot$min^{-1})	P (MPa)	D_{12} (10^{-9} m$^2\cdot$s^{-1})	F (cm$^3\cdot$min^{-1})	P (MPa)	D_{12} (10^{-9} m$^2\cdot$s^{-1})	F (cm$^3\cdot$min^{-1})
0.00	0.1	2.49 ± 0.02	0.20	0.1	3.38 ± 0.04^{a}	0.19	0.1	4.46 ± 0.07	0.21	0.1	5.55 ± 0.04	0.20
				0.1	3.39 ± 0.05^{b}	0.19						
				0.1	$3.35 \pm 0.03^{b,d}$	0.10						
				0.1	3.38 ± 0.05^{c}	0.19						
	8.8	2.44 ± 0.02	0.19	9.5	3.27 ± 0.01	0.19	8.1	4.29 ± 0.05	0.19	8.7	5.40 ± 0.04	0.19
		2.38 ± 0.03	0.19					4.25 ± 0.05	0.19			
0.20				0.1	2.14 ± 0.04	0.19	0.1	3.16 ± 0.05	0.19			
0.40	0.1	1.22 ± 0.01	0.20	0.1	1.86 ± 0.05	0.20	0.1	2.63 ± 0.04	0.20	0.1	3.65 ± 0.03	0.20
0.60	0.1	1.26 ± 0.02	0.20	0.1	1.93 ± 0.02	0.20	0.1	2.67 ± 0.05	0.20	0.1	3.49 ± 0.07	0.20
	8.3	1.19 ± 0.01	0.20	7.6	1.77 ± 0.03	0.20	8.2	2.49 ± 0.03	0.20	8.4	3.32 ± 0.02	0.20
	17.8	1.14 ± 0.02	0.20	17.8	1.55 ± 0.01	0.20	16.3	2.38 ± 0.01	0.20	16.9	3.16 ± 0.04	0.20
0.80	0.1	1.43 ± 0.03	0.19	0.1	2.18 ± 0.04	0.20	0.1	3.01 ± 0.06	0.20	0.1	4.03 ± 0.07	0.21
	8.0	1.39 ± 0.02	0.19	8.7	2.05 ± 0.02	0.19	8.4	2.81 ± 0.01	0.19	8.7	3.74 ± 0.02	0.19
	16.3	1.37 ± 0.02	0.18	16.2	1.94 ± 0.01	0.19	16.3	2.69 ± 0.02	0.19	16.3	3.67 ± 0.04	0.19
1.00	0.1	2.13 ± 0.01	0.19	0.1	3.18 ± 0.03	0.20	0.1	4.54 ± 0.03	0.20	0.1	5.96 ± 0.08	0.21
	7.8	2.09 ± 0.02	0.19	8.0	2.91 ± 0.02	0.19	7.8	4.09 ± 0.05	0.19	8.1	5.30 ± 0.05	0.19
	16.1	1.94 ± 0.01	0.19	15.8	2.76 ± 0.04	0.19	15.8	3.83 ± 0.06	0.19	15.8	5.04 ± 0.03	0.19
	24.4	1.86 ± 0.01	0.19	24.0	2.67 ± 0.01	0.19	24.2	3.64 ± 0.01	0.19	24.5	4.78 ± 0.01	0.19

[a] Five percent concentration (volume toluene/volume acetonitrile) of the injected solutions.
[b] Ten percent concentration (volume toluene/volume acetonitrile) of the injected solutions.
[c] Twenty percent concentration (volume toluene/volume acetonitrile) of the injected solutions.
[d] Flow rate, 0.1 cm$^3\cdot$min^{-1}.

mixture was investigated. Results for the equimolar mixture are given in Table III, where each result is the average of four or five measurements. It is seen that D_{12} is constant, within the estimated uncertainties, over this wide concentration range of the injected solution. The actual mole fractions of hexane in the injected solutions were 0.38, 0.74, and 1.0, where the mobile phase mole fractions were 0.25, 0.50, and 0.75. For the pure liquid mobile phases, the injected solutions were generally of solute concentration 10% (v/v). In the case of the toluene + acetonitrile system, the mole fractions of acetonitrile in the injected solutions were 0.32, 0.51, and 1.0, corresponding to mobile phase mole fractions of 0.2, 0.4, and 0.8. For the mobile phase with 0.4 mole fraction of toluene, the injected solution had a mole fraction of 0.44 of toluene. For toluene diffusing in pure acetonitrile, and vice versa, the solute concentration in the injected sample was 10%

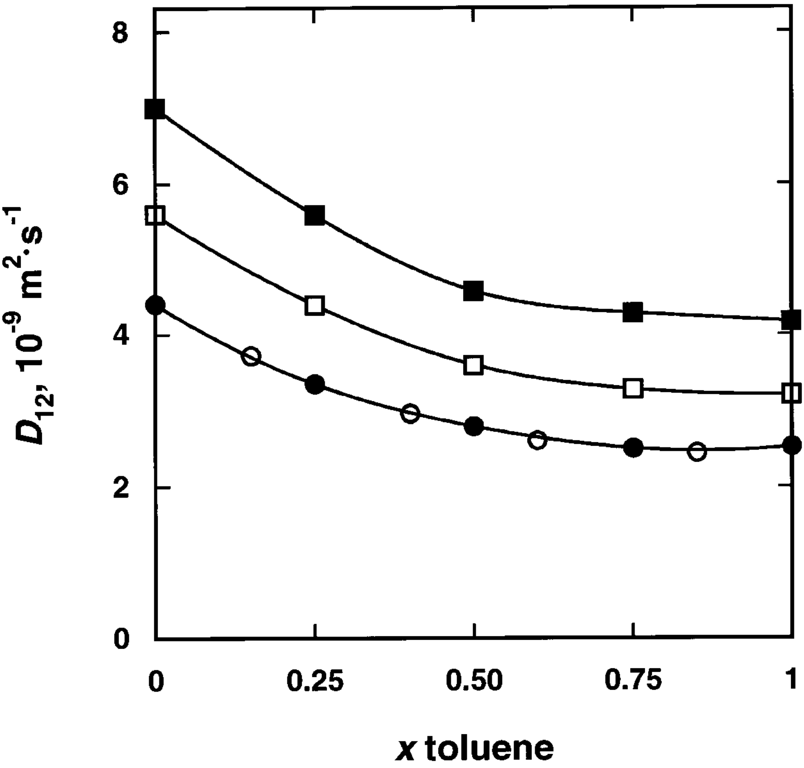

Fig. 2. Dependence of the mutual diffusion coefficient on the mole fraction of toluene for toluene + *n*-hexane mixtures at atmospheric pressure. (●) 299.2 K; (□) 323.2 K; (■) 348.2 K. (○) Ghai and Dullien [27], 298.15 K.

(v/v). This is equivalent to 0.05 mole fraction of toluene in the former case and 0.18 mole fraction of acetonitrile in the latter case.

To investigate the effect of increased pressure on the diffusion tube diameter, D_{12} was measured for toluene in *n*-hexane at 299.2 K at atmospheric pressure and the system then pressurized to 30 MPa for several hours. After reduction of the pressure to atmospheric pressure, D_{12} was remeasured. The constancy of the result indicated that there had been no permanent distortion of the tube on pressurization.

In practice, it was found that flow rates above $0.2\,\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ were sometimes required to maintain a constant high pressure in the coil using this crimped capillary. To reduce the effect of secondary flow, coil A, with the larger helical radius, was subsequently used. The normalized flow rate was less than 1 to stay within the range for which the equation of Nunge et al. [11] works quite well.

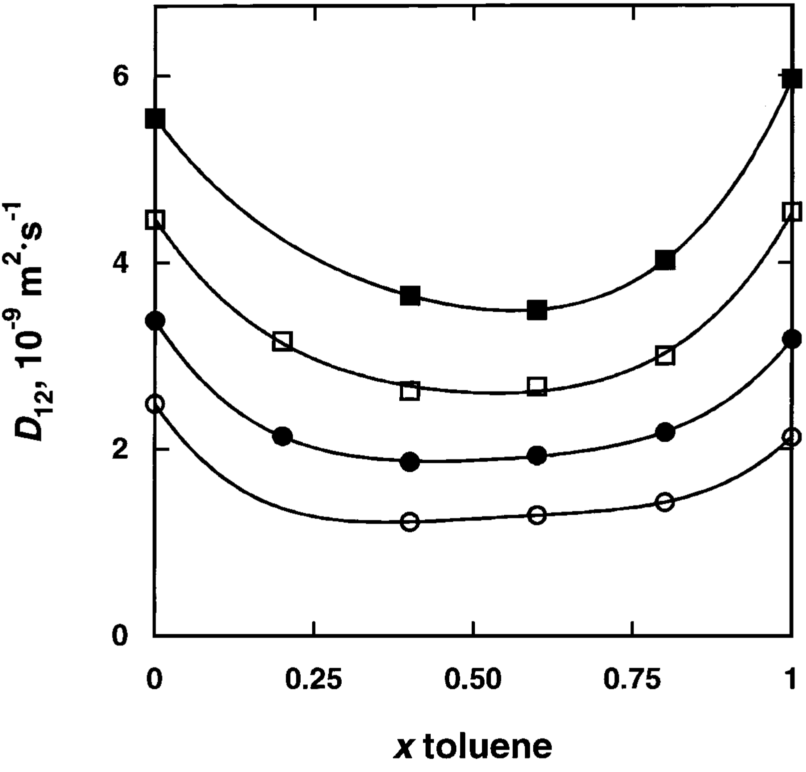

Fig. 3. Dependence of the mutual diffusion coefficient on the mole fraction of toluene for toluene + acetonitrile mixtures at atmospheric pressure. (○) 273.2 K; (●) 298.2 K; (□) 323.2 K; (■) 348.2 K.

4. RESULTS

D_{12} values, measured with coil A using the refractomonitor as detector, and corrected for secondary flow as described above, are reported for x toluene + $(1-x)$ n-hexane mixtures in Table IV and for x toluene + $(1-x)$ acetonitrile mixtures in Table V at different mobile phase compositions in the temperature range 299.2 to 348.2 K for the first system and 273.2 to 348.2 K for the second system, at pressures up to 25 MPa. The values given are the averages of a minimum of four, and usually five or six, measurements. The standard deviations are given. The dependence of D_{12} on the composition of the mobile phase at the different temperatures is shown for these two systems in Figs. 2 and 3. The pressure dependence of D_{12} on the composition of the mobile phase is shown for these two systems

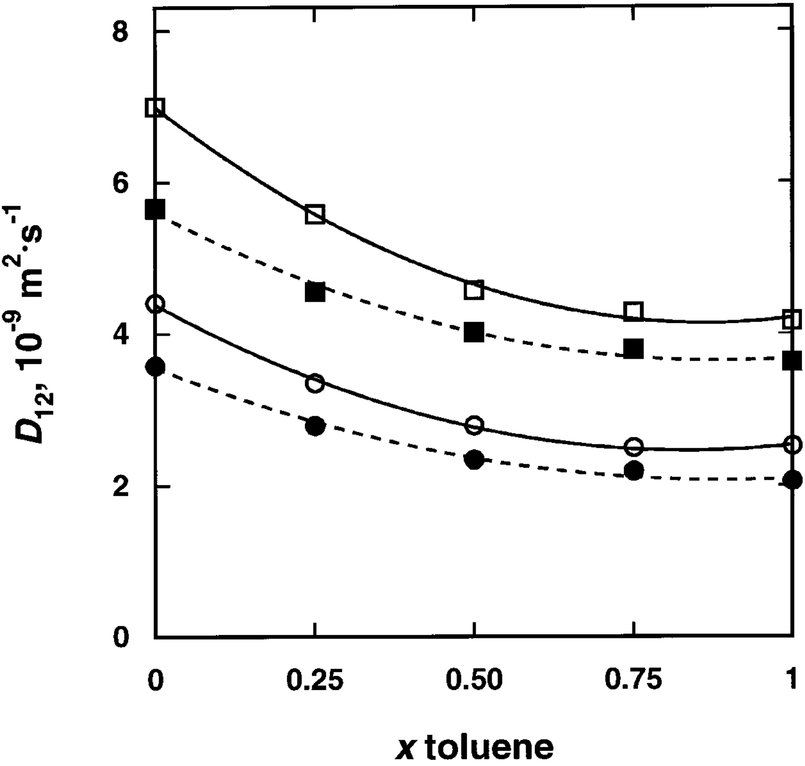

Fig. 4. Dependence of the mutual diffusion coefficient on the mole fraction of toluene for toluene + n-hexane mixtures at different pressures. (○) 0.1 MPa at 299.2 K; (●) 22 MPa at 299.2 K; (□) 0.1 MPa at 348.2 K; (■) 22 MPa at 348.2 K.

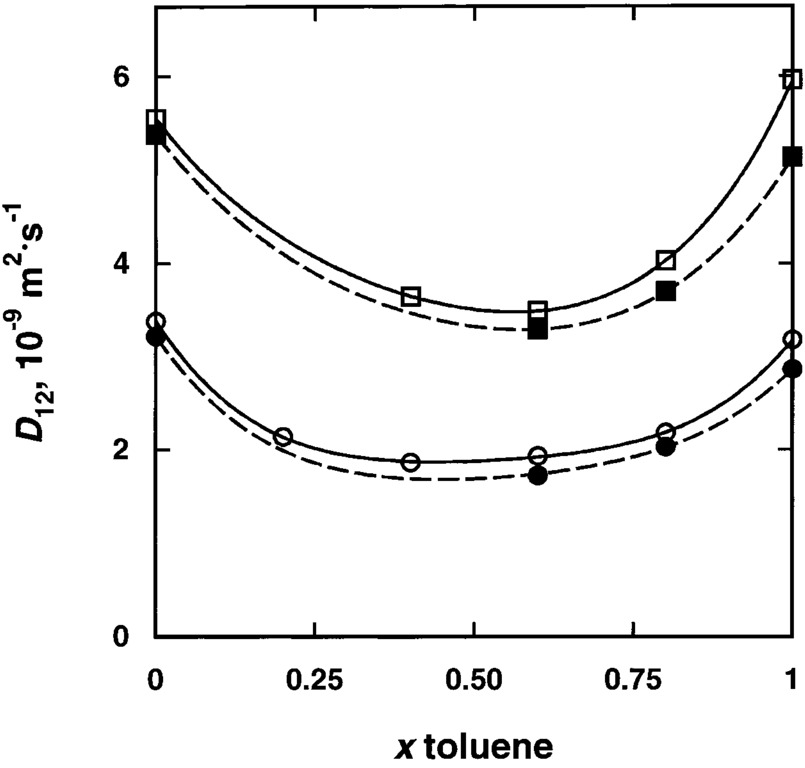

Fig. 5. Dependence of the mutual diffusion coefficient on the mole fraction of toluene for toluene + acetonitrile mixtures at different pressures. (○) 0.1 MPa at 298.2 K; (●) 10 MPa at 298.2 K; (□) 0.1 MPa at 348.2 K; (■) 10 MPa at 348.2 K.

in Figs. 4 and 5. The pressure dependence is well represented by the equation

$$D_{12} = be^{-\alpha P} \tag{4}$$

The value derived for α varies slightly with the composition of the mixture and the temperature but is about $0.8 \times 10^{-8}\, \mathrm{m^2 \cdot N^{-1}}$ for each of these systems. This corresponds to a fractional decrease in diffusion coefficient of about 0.8% per MPa, a figure slightly lower than that found (0.9 to 1.0%) for larger molecules diffusing in *n*-hexane and *n*-decane [11].

5. DISCUSSION

D_{12} values have been reported previously [27] for toluene + *n*-hexane mixtures at 298.15 K over the complete composition range at ambient pressure. As shown in Fig. 2, the present measurements at 299.2 K are on average 1% higher than these literature values, which is the difference to be expected from the temperature coefficient of D_{12}. The maximum difference between the two sets of data is only 1.6%. Trace diffusion coefficient measurements have been reported [6] for ^{14}C-benzene and ^{14}C-toluene in *n*-hexane at 298.2 K at pressures up to 400 MPa. For comparison purposes, values of D_{12} have been interpolated at the experimental pressures of this work from plots of log D_{12} against pressure. For toluene in *n*-hexane, the present measurements for D_{12} values agree with values interpolated from these literature data within the combined estimated uncertainties. The maximum deviation was 5.7% at 16.8 MPa. As a further check on the accuracy of the present measurements at elevated pressures, D_{12} measurements were also made for benzene in *n*-hexane at pressures of 5.2, 10.0, and 20.2 MPa. The results ($10^{-9}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$) were 4.55 ± 0.04, 4.36 ± 0.04, and 4.07 ± 0.14, in excellent agreement with the interpolated intradiffusion coefficient values ($10^{-9}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$) from the literature [6] of 4.54, 4.38, and 4.07 at these respective pressures.

A direct comparison between the present data for toluene in *n*-hexane [12] and other measurements by the chromatographic peak broadening method which were reported [13] for a pressure of 16 MPa is shown in Fig. 6. The agreement is very satisfactory. The overall comparison indicates that it is reasonable to assign an uncertainty of less than 4% to the present measurements.

The plots of D_{12} against mole fraction of toluene shown in Figs. 2 and 3 for toluene + *n*-hexane and toluene + acetonitrile mixtures show negative deviations from straight-line behavior, with greater deviations for the toluene + acetonitrile system. Similar behavior is evident at higher pressure as shown in Fig. 4 for toluene + *n*-hexane, where the D_{12} values obtained by interpolation at 22 MPa are compared with atmospheric pressure data.

A widely used expression for the mutual diffusion coefficient is the Darken equation [30, 31],

$$D_{12} = (x_1 D_1^* + x_2 D_2^*)\,\beta \tag{4}$$

which relates the mutual diffusion coefficient to the intradiffusion (tracer) coefficients at x_1 and x_2 and the thermodynamic factor, β, given by $[(\partial \ln a/\partial \ln x)]_{T,P}$, where a is the activity and x the mole fraction, which has the same value for each component. In the absence of tracer diffusion coefficient data on these mixtures, modifications to this equation have been proposed which involve the mutual diffusion coefficient values at infinite dilution, D^0_{AB}, for example [32],

$$D_{12} = (x_1 D^0_{21} + x_2 D^0_{12})\,\beta \tag{5}$$

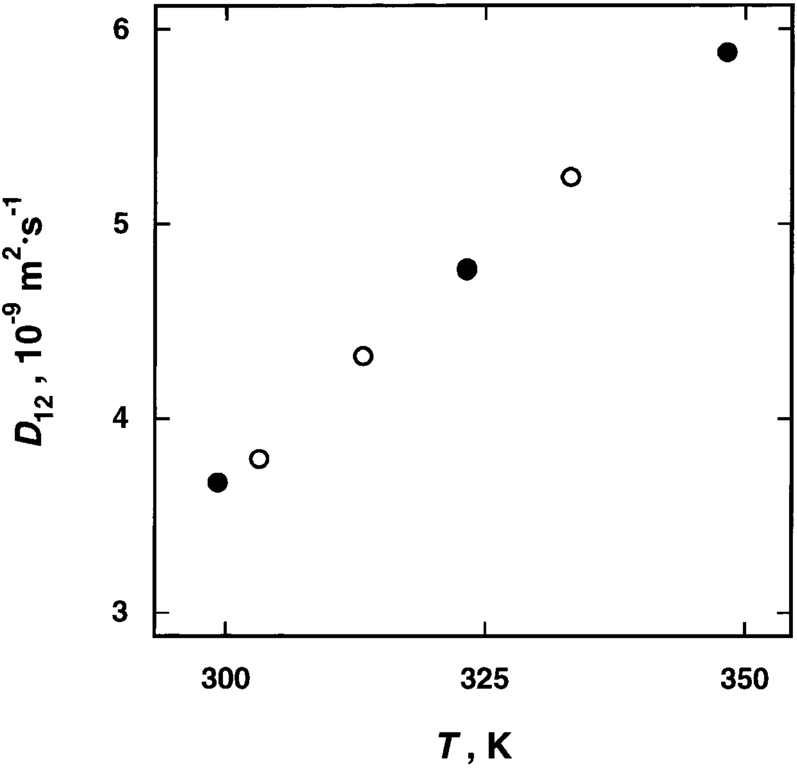

Fig. 6. Comparison of mutual diffusion coefficient data for toluene at infinite dilution in n-hexane at 16 MPa. (●) Present measurements; (○) Ref. 13.

Values for the thermodynamic factor have been calculated from excess free energy data for mixtures of toluene + n-hexane and toluene + acetonitrile [33, 34] at 313.2 and 343.2 K, respectively, fitted to a three-suffix Margules equation, and values for D_{12} calculated at the closest temperatures. It is found that for mixtures of toluene + n-hexane, where the thermodynamic factor is about 0.8, the experimental D_{12} values are consistently about 6% higher than the calculated values. This is similar to the discrepancy previously noted by Ghai and Dullien [27] by application of the Darken equation for this system. The system toluene + acetonitrile is less ideal, with higher positive excess free energies than for the corresponding toluene + n-hexane mixtures. The calculated thermodynamic factor is found to have the values 0.50, 0.48, and 0.56 for mixtures with toluene mole fractions of 0.4, 0.6, and 0.8, respectively. The experimental D_{12} values are consistently 27% higher than the values calculated from Eq. (5).

Chhabra [14] has shown that high pressure self-diffusion data for similar nonpolar liquids can be satisfactorily represented in terms of the formulation of Dullien [35]:

$$\delta = [2\eta VD/RT]^{1/2} \tag{6}$$

where δ is the average momentum transfer distance, η is the shear viscosity, V is the molar volume, D is the self-diffusion coefficient, and R is the gas constant. Although this equation is not based on any particular model of the liquid state, it describes the temperature dependence of self-diffusion coefficients in simple liquids and molten metals very satisfactorily [36, 37]. This equation has been applied to the present mutual diffusion coefficient data for the toluene + n-hexane system, using reported viscosity data

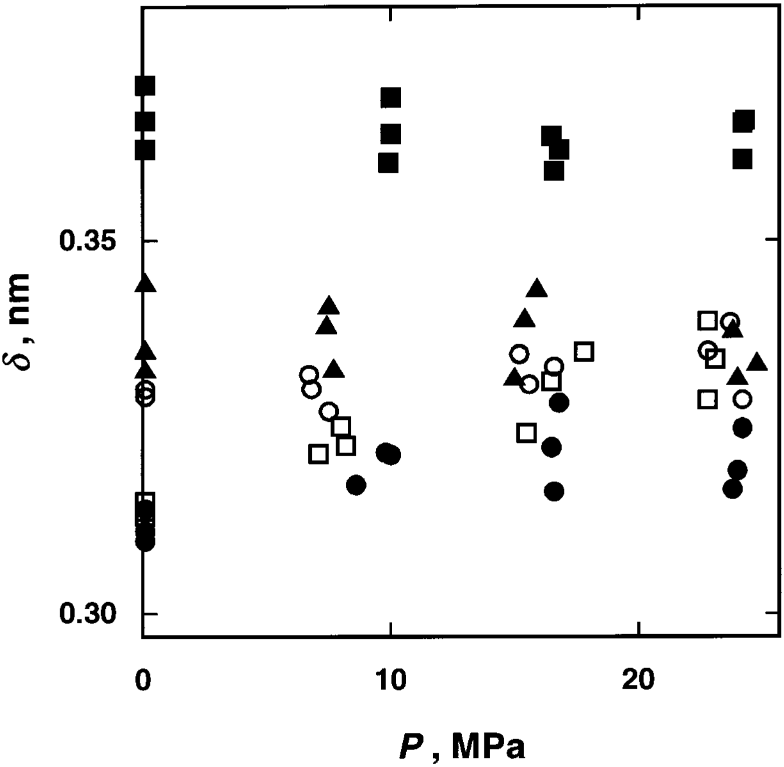

Fig. 7. Variation of δ with pressure for toluene + n-hexane mixtures at different mole fractions of toluene: (■) ~0; (○) 0.25; (●) 0.50; (□) 0.75; (▲) ~1.

[38, 39], to provide a further test of the applicability of this equation for pure liquids and, also, to see whether it can satisfactorily correlate the mixture data also. The resulting values for δ are plotted in Fig. 7, which shows that δ is essentially independent of temperature and pressure for these mixtures. A similar conclusion had been reached by Chhabra [14] for pure nonpolar liquids. The variation of δ with mole fraction is illustrated in Fig. 8, in which the values for δ for the toluene + acetonitrile mixtures are included. The viscosities for this system were taken from the literature [38, 40]. By construction of smooth curves through the points, it is possible to calculate mutual diffusion coefficients from Eq. (6) for any composition at any temperature from a knowledge of the mixture viscosity and density.

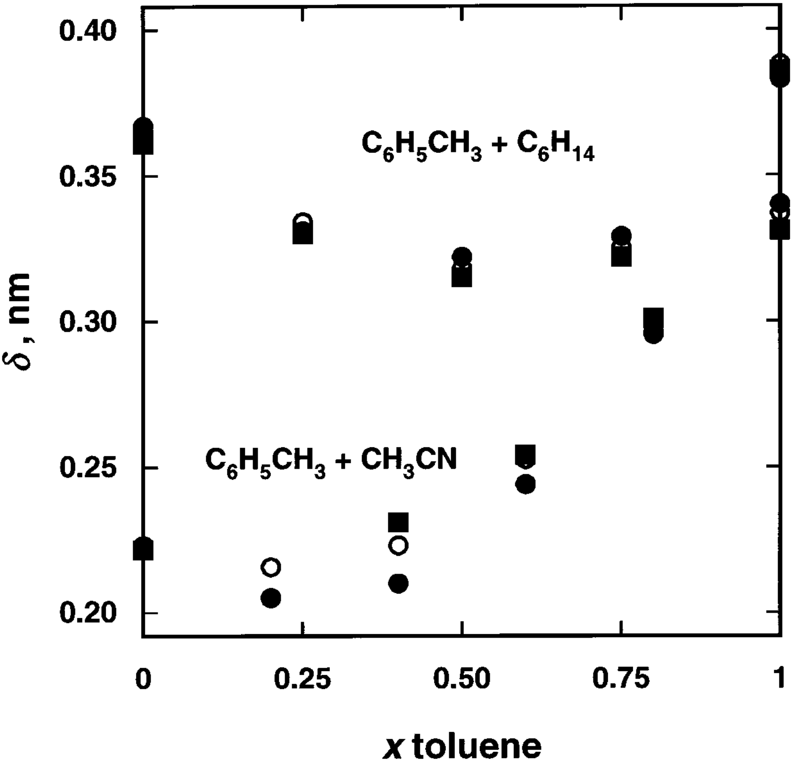

Fig. 8. Variation of δ averaged over the values for different pressures versus mole fraction at different temperatures for the two systems. (●) 299.2 K (298.2 K); (○) 323.2 K; (■) 348.2 K.

5.1. Hard-Sphere Theory

The mutual diffusion coefficient for a binary mixture of rough hard spheres is given [9] by

$$D_{12} = \frac{3(kT)^{1/2}}{8n_{12}\sigma_{12}^2} \left[\frac{m_1 + m_2}{2\pi m_1 m_2}\right]^{1/2} \frac{A_{12}}{g_{12}(\sigma)} \left(\frac{D}{D_{\mathrm{E}}}\right)_{\mathrm{MD}} \tag{7}$$

where n_{12} is the total number density $(n_1 + n_2)$, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ for spheres of diameter σ_i, m_1 and m_2 are molecular masses, and $(D/D_{\mathrm{E}})_{\mathrm{MD}}$ is the computed correction to the Enskog value to allow for correlated molecular motion. A_{12} is the translational–rotational coupling constant and g_{12} is the unlike radial distribution function, given in terms of the like distribution functions by the expression,

$$g_{12} = [\sigma_2 g_{11} + \sigma_1 g_{22}]/2\sigma_{12} \tag{8}$$

where g_{ii} is given by

$$g_{ii} = 1/(1-\xi) + 3Y/[2(1-\xi)]^2 + Y_i^2/[(2(1-\xi)]^3 \tag{9}$$

and $\xi = \xi_1 + \xi_2$, with ξ_i equal to $\pi n_i \sigma^3/6$ and $Y_i = (\sigma_i \xi_j + \sigma_j \xi_i)/\sigma_j$.

The calculation of D_{12} for a hard-sphere mixture requires values for σ_i, for $(D/D_{\mathrm{E}})_{\mathrm{MD}}$, and for A_{12}. Core sizes of solute and solvent molecules are derived from fitting viscosity data [4, 38–40], and are given in Table VI. Corrections to Enskog theory are interpolated from computed molecular dynamics calculations [41, 42] allowing for correction to an infinite-sized system. Values for the coupling factor A_{12} are then determined by fitting experimental mutual diffusion measurements. We restrict our attention to the limiting case where one of the components is present at a trace concentration, for which the corrections to Enskog theory are more accurately known. The results are presented in Table VII.

Table VI. Molecular Core Sizes

	σ (nm) at T (K)		
Compound	298.15	323.15	348.15
n-Hexane	0.566	0.564	0.562
Toluene	0.549	0.547	0.545
Acetonitrile	0.409	0.406	0.403

Table VII. Translational–Rotational Coupling Constants from Limiting Mutual Diffusion Coefficient Measurements for Toluene + n-Hexane

T (K)								
299.15			323.15			348.15		
P (MPa)	$(D/D_{\mathrm{E}})_{\mathrm{MD}}$	A_{12}	P (MPa)	$(D/D_{\mathrm{E}})_{\mathrm{MD}}$	A_{12}	P (MPa)	$(D/D_{\mathrm{E}})_{\mathrm{MD}}$	A_{12}
Toluene in n-hexane								
0.1	0.96	0.86	0.1	1.09	0.81	0.1	1.17	0.81
10.0	0.91	0.86	10.0	1.04	0.80	9.9	1.14	0.76
16.8	0.88	0.84	16.5	1.01	0.80	16.6	1.12	0.75
24.2	0.84	0.87	24.3	0.99	0.80	24.2	1.10	0.75
n-Hexane in toluene								
0.1	0.57	1.28	0.1	0.74	1.08	0.1	0.89	0.99
7.5	0.58	1.20	7.4	0.71	1.12	7.7	0.86	1.01
15.9	0.51	1.32	15.4	0.68	1.14	15.0	0.82	1.02
24.8	0.48	1.30	23.8	0.65	1.16	24.0	0.79	1.04
298.15 K								
Toluene in acetonitrile								
0.1	1.09	0.84	0.1	1.27	0.78	0.1	1.36	0.76
9.5	1.08	0.85	8.1	1.18	0.83	8.7	1.34	0.78
Acetonitrile in toluene								
0.1	0.57	0.84	0.1	0.65	0.89	0.1	0.76	0.85
8.0	0.56	0.79	7.8	0.64	0.83	8.1	0.73	0.81
15.8	0.55	0.78	15.8	0.63	0.81	15.8	0.71	0.81
24.8	0.52	0.77	23.8	0.62	0.80	24.0	0.69	0.80

The A_{12} values show a small temperature dependence for these systems, except for n-hexane in toluene, where the effect is greater. In all cases, there is a very weak pressure dependence, which makes possible the reliable calculation of mutual diffusion coefficients at infinite dilution for these systems at higher pressures and, by interpolation, also at other temperatures. For toluene in n-hexane, A_{12} decreased from 0.86 at 299.2 K to 0.76 at 348.2 K. The 299.2 K value is higher than that obtained previously [9], as a result of changes in the core sizes which resulted from subsequent fitting of more extensive transport property data. Similar values were given for toluene in acetonitrile, where A_{12} decreased from 0.84 at 298.2 K to 0.77 at 348.2 K. For acetonitrile in toluene, there was a slight increase, from

0.80 to 0.82, over this temperature range. The points at 273.2 K were not included, as V/V_0 was less than 1.5, the point at which the hard-sphere system becomes metastable. These results suggest that the high dipole moment of acetonitrile has no specific effect on the mutual diffusion in a very weakly polar solvent. A similar conclusion had been reached earlier [43] in the case of nonpolar liquids plus chlorinated alkanes, which possess smaller dipole moments. Significantly smaller values for A_{12} have been derived for systems where there are strong dipole–dipole interactions, as in acetonitrile + methanol mixtures, or quadrupole–dipole interactions, as in carbon disulfide plus acetonitrile mixtures [44].

In view of the near-constancy of the A_{12} values noted above, it is surprising that A_{12} is higher for hexane in toluene, with values ranging from 1.28 at 299.2 K to 1.01 at 328.2 K. It has been suggested [45] that a larger A_{12} might arise where the substance at trace concentration consists of elongated molecules such as *n*-hexane. Again, these values are pressure independent over this range, which allows reliable calculation of mutual diffusion coefficients at infinite dilution at other temperatures and pressures.

6. CONCLUSIONS

Mutual diffusion coefficients for toluene + *n*-hexane and toluene + acetonitrile mixtures are reported for the temperature range 273.2 to 348.2 K at pressures up to 25 MPa, with an uncertainty which is estimated to be less than ±4%. The fractional decrease in D_{12} is about 0.8% per MPa increase in pressure, for the two systems studied. Both systems show negative deviations from a linear dependence of D_{12} on mole fraction, at all temperatures and pressures.

The Dullien formulation can be used for calculation of mutual diffusion coefficients for liquids and their mixtures at different compositions, and at different temperatures and pressures, from viscosity and density data at the given thermodynamic state and a knowledge of the mutual diffusion coefficient under one set of conditions.

Application of the rough hard-sphere theory to mutual diffusion at infinite dilution shows that the translational–rotational coupling constants are pressure independent.

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