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Transport Properties of Nonelectrolyte Liquid Mixtures. X. Limiting Mutual Diffusion Coefficients of Fluorinated Benzenes in *n*-Hexane

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Mutual diffusion coefficients, D_{12}, have been measured for benzene, seven fluorinated benzenes, and octafluorotoluene diffusing in *n*-hexane at trace concentration in the temperature range 213.2–333.2 K by the chromatographic peak-broadening technique with an estimated accuracy of ±2.5%. These results are compared with the predictions of rough hard-sphere theory (RHS). The results are reproducible to within ±10% with the translational–rotational coupling factor equal to the value for the solvent. The activation energy of diffusion E_D, computed from Arrhenius plots, is almost constant for these solutes.

KEY WORDS: Enskog theory; fluorinated benzenes; *n*-hexane; mutual diffusion coefficient; Taylor dispersion; translational–rotational coupling.

1. INTRODUCTION

A study of transport properties is extremely important both experimentally, to obtain precise measurements on systems of industrial importance, and on key systems for testing theories, and theoretically, to provide information on the least well-understood state of matter, the liquid state.

The theory of transport phenomena is well developed for dilute gases made up of structureless spherical particles [1]. Accurate prediction of diffusion, viscosity, and thermal conductivity is possible, provided that the

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potential energy functions are known. However, for dense fluids, problems arise because of many-body effects. Also, the aspherical shape of the molecules leads to translational–rotational coupling. The computer simulation technique of molecular dynamics has limitations for transport-property calculations, because the potential energy functions are not accurately known and the computational time is long for viscosity and thermal conductivity. In view of these difficulties in calculating exactly the transport properties of dense fluids and their mixtures, it is necessary to use empirical methods or, preferably, semiempirical methods which are based on theory. In this paper, rough hard-sphere theory (RHS) is used to fit the measured D_{12} for benzene, *o*-difluorobenzene, *p*-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,3,5- and 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, hexafluorobenzene, and octafluorotoluene diffusing at trace concentrations in *n*-hexane in the temperature range 213.2–333.2 K.

2. MATERIALS

HPLC-grade *n*-hexane and the fluorinated solutes (purity, 98–99%) were purchased from Aldrich Chemical Co. Ltd., Gillingham, England, with the exception of 1,2,4-trifluorobenzene (pure), which was obtained from Koch-Light Laboratories, Colinbrook, England. Benzene (99.9%) was purchased from Aldrich Chemical Co. Ltd., Poole, England. Refractive-index measurements were made using a high-accuracy 60/ED Abbé refractometer (Bellingham and Stanley, England). The agreement with literature values was very satisfactory. These liquids were used as received without further purification. However, *n*-hexane was degassed by distillation prior to use.

3. EXPERIMENTS

Interdiffusion coefficient measurements were made for fluorinated benzenes diffusing in *n*-hexane at trace concentrations in the range 213.3–333.2 K by the chromatographic peak-broadening technique (Taylor dispersion technique) [2, 3]. Dilute solutions ($\leqslant 0.1\%$, v/v) of the aromatic compounds in *n*-hexane were prepared and 10-μl amounts were injected with a Rheodyne syringe loading sample injector, Model 7125, with a 10-μl sample loop into the flowing solvent. This was pumped at a fixed volume flow rate of 0.1 ml min^{-1}, which was found to be low enough to give the true diffusion coefficient values, by an Altex Model 110A metering pump through the diffusion tube. This consisted of a 20.40-m length of 0.0383-cm-i.d. (loop A), or a 29.96-m length of 0.0405-cm-i.d. (loop B), 316 stainless-steel tubing, obtained from Phase Separation Ltd. Clwyd, UK. Loops A and B were wound in the form of a helix with radii of 11.4 and 4.85 cm, respectively, and were immersed in a Townsen and Mercer Series III thermostat bath containing water for temperatures above 273.3 K and a crushed ice–water mixture for measurements at 273.2 K. The temperature control was better than 0.02 K and measured with mercury-in-glass thermometers calibrated at the National Physical Laboratory, Teddington, England. Temperatures below 273.2 K were attained by a bridge-controlled Minus Seventy thermostat bath (Townsen and Mercer, Series III), containing methylated spirit–Cardice (dry ice) mixtures [4, 5]. The temperature control in this range was better than 0.05 K and was measured with a Lauda R46 digital thermometer. The concentration profile was monitored by an Altex Model 153 UV detector with a 254-nm filter and recorded on a variable-speed Tekman electronic recorder.

The theory of the Taylor dispersion technique has been described in detail in the literature [2, 3, 6–8]. With a suitable choice of experimental conditions, the mutual diffusion coefficient for the liquid mixtures can be calculated from the variance σ^2 of the Gaussian recorder trace of the distribution of the solute by using the expression

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

where R_0 is the internal radius of the diffusion tube and t is the dispersion time of the solute in the tube. Because of possible nonuniformities in the tube bore, the apparatus constant ($R_0^2/24$) was determined by comparison of the measured variance at a low solvent flow rate with the known mutual diffusion values for some specific systems, where D_{12} was in the range of the values expected in this study.

Errors in the derived diffusion coefficients arising from the determination of the variance of the dispersion peak, from the small variations in the volume flow rate, and from the uncertainties in the apparatus constant and possible uncertainties due to tube end effects have been estimated as 2.5% maximum.

4. RESULTS

Experimentally determined D_{12} values at a nominal solvent flow rate of 0.1 ml · min^{-1} for different solute–solvent pairs in the temperature range 273.2–348.2 K are listed and compared with literature values in Table I. A refractomonitor was employed where the solute was nonaromatic. The

Table I. Comparison of Measured Diffusion Coefficients with Literature Values

			D_{12} (10^{-9} $m^2 \cdot s^{-1}$)		
				Measured	
Solute	Solvent	T(K)	Literature	Loop A	Loop B
Benzene	*n*-Hexane	273.7	3.40 [9]	3.45	—
		299.2	4.66 [9]	4.71	4.66
		299.2	4.747 [10]	4.69	4.72
		299.2	4.758 [11]	4.74	—
		299.2	4.723 [12]	4.70	—
		313.2	6.82 [9]	—	6.96
		313.2	7.01 [13]	—	—
		333.2	5.47 [9]	5.53	—
Toluene	*n*-Hexane	273.2	3.21 [9]	3.22	—
		299.2	4.38 [9]	4.45	4.40
		299.2	4.344 [14]	—	—
		299.2	4.355 [14]	—	—
		313.2	5.00 [9]	4.95	—
n-Hexane	Toluene	299.2	2.479 [14]	2.52	2.48
		300.2	2.41 [15]	—	—
		323.2	3.25 [15]	3.21	3.30
n-Decane	Toluene	299.2	1.87 [15]	1.86	1.82
		323.2	2.41 [15]	2.52	2.51
		348.2	3.21 [15]	3.25	3.20
n-Tetradecane	Toluene	299.2	1.45 [15]	1.47	1.45
		323.2	1.97 [15]	1.98	1.99
		348.2	2.61 [15]	2.61	2.60

injected solute may have a concentration up to 10% (v/v) where solute and solvent refractive indices were comparable. The D_{12} values are in good agreement, generally well within the combined estimated uncertainties. D_{12} values for benzene and eight fluorinated benzenes in *n*-hexane in the temperature range 213.2–333.2 K are reported in Table II, as the mean of five measurements.

Table II. Mutual Diffusion Coefficients of Organic Solutes in *n*-Hexane

Compound	D_{12} (10^{-9} m$^2 \cdot$ s^{-1})[a]						
	213.2 K	233.2 K	253.2 K	273.2 K	299.2 K	313.2 K	333.2 K
Benzene	1.21 ± 0.01 (g)	1.80 ± 0.03 (c)	2.57 ± 0.03 (c)	3.43 ± 0.08 (a) 3.45 ± 0.02 (a) 3.40 ± 0.04 (b)	4.73 ± 0.06 (h) 4.66 ± 0.04 (i)	5.53 ± 0.05 (i) 5.57 ± 0.01 (a) 5.61 ± 0.01 (j)	6.96 ± 0.10 (m)
o-Difluorobenzene	1.10 ± 0.03 (c)	1.60 ± 0.08 (c)	2.41 ± 0.02 (c)	3.35 ± 0.04 (a) 3.26 ± 0.03 (b)	4.48 ± 0.06 (h) 4.44 ± 0.03 (k)	5.23 ± 0.01 (a) 5.29 ± 0.08 (h)	6.61 ± 0.20 (m)
p-Difluorobenzene	1.10 ± 0.03 (c)	1.72 ± 0.11 (c)	2.49 ± 0.02 (c)	3.36 ± 0.06 (a)	4.63 ± 0.03 (l) 4.63 ± 0.07 (k)	5.51 ± 0.07 (a) 5.37 ± 0.06 (b)	6.62 ± 0.03 (c)
1,2,4-Trifluorobenzene	1.18 ± 0.09 (c)	1.72 ± 0.03 (c)	2.33 ± 0.03 (c)	3.20 ± 0.04 (c) 3.21 ± 0.02 (b)	4.43 ± 0.06 (h), 4.49 ± 0.02 (m) 4.39 ± 0.05 (b)	5.29 ± 0.04 (b) 5.16 ± 0.05 (c)	6.34 ± 0.06 (c)
1,2,3,5-Tetrafluorobenzene	1.05 ± 0.02 (c)	1.67 ± 0.03 (c)	2.27 ± 0.08 (c)	3.29 ± 0.06 (b) 3.42 ± 0.02 (d)	4.40 ± 0.05 (d), 4.57 ± 0.01 (b) 4.41 ± 0.07 (n)	5.00 ± 0.09 (b) 4.91 ± 0.07 (c)	6.48 ± 0.06 (c)
1,2,4,5-Tetrafluorobenzene	1.05 ± 0.02 (c)	1.68 ± 0.05 (c)	2.22 ± 0.03 (c)	3.17 ± 0.05 (d) 3.15 ± 0.05 (b)	4.42 ± 0.08 (d) 4.26 ± 0.04 (b) 4.49 ± 0.04 (e)	5.28 ± 0.04 (b) 5.17 ± 0.09 (c) 4.99 ± 0.06 (d)	6.20 ± 0.08 (c)
Pentafluorobenzene	1.06 ± 0.04 (c)	1.70 ± 0.02 (c)	2.26 ± 0.04 (c)	2.98 ± 0.01 (b)	3.99 ± 0.01 (o), 4.02 ± 0.04 (d) 4.02 ± 0.04 (p), 4.06 ± 0.08 (q)	4.83 ± 0.08 (b)	5.95 ± 0.07 (c)
Hexafluorobenzene	1.01 ± 0.02 (c)	1.62 ± 0.03 (c)	2.16 ± 0.03 (c)	2.87 ± 0.01 (e) 2.82 ± 0.09 (b)	4.00 ± 0.04 (r), 4.08 ± 0.03 (s) 4.10 ± 0.01 (t), 4.03 ± 0.05 (m)	4.62 ± 0.09 (e)	5.81 ± 0.10 (c)
Octafluorotoluene	0.88 ± 0.01 (c)	1.40 ± 0.06 (c)	1.83 ± 0.02 (c)	2.51 ± 0.02 (f) 2.45 ± 0.04 (b)	3.48 ± 0.06 (u), 3.51 ± 0.03 (e) 3.52 ± 0.03 (a), 3.45 ± 0.05 (n)	4.07 ± 0.02 (j)	4.98 ± 0.01 (c)

[a] (a) = (1%, R. A), (b) = (0.1%, H, A), (c) = (0.05%, L, B), (d) = (10%, R. A), (e) = (5%, R, A), (f) = (0.05%, H, B), (g) = (0.5%, L, B), (h) = (1%, R, B), (i) = (0.5%, R, A), (j) = (1.5%, R, A), (k) = (0.05%, H, A), (l) = (2%, R, B), (m) = (0.1%, L, A), (n) = (0.5%, L, B), (o) = (8%, R, A), (p) = (6%, R, A), (q) = (0.2%, L, B), (r) = (5%, R, B), (s) = (10%, R, B), (t) = (30%, R, B), and (u) = (3%, R, A) where the first figure is the concentration of injected solution, R stands for refractomonitor, A and B for loop A or B, and H and L for high-pressure cell or low-pressure cell in the UV detector.

5. DISCUSSION

Extension of the Eyring theory of reaction rates [16] leads to the interpretation of diffusion-coefficient data in terms of an activation energy of diffusion E_D, which is due to the caging of the solute molecules by solvent molecules (configurational activation energy) and back scattering (back-scattering activation energy). The configurational activation energy increases with solute-to-solvent size ratio, reflecting the fact that larger molecules have more nearest-neighbor solvent molecules around them and therefore there is a gretaer probability of binary collisions between solute and solvent molecules. Thus, it is more difficult for larger molecules to escape from a cage of solvent molecules. The back-scattering activation energy depends upon the solute-to-solvent mass ratio. As the solute molecule becomes heavier, back scattering diminishes.

Values of E_D were calculated from the slope of plots of log D_{12} against the reciprocal of the absolute temperature in the range 213.2–333.2 K and are tabulated in Table III. The values are remarkably similar. These can be contrasted with the calculated activation energies for diffusion for *n*-hexane in toluene and for toluene in *n*-hexane, which show that E_D is larger for the former case (12.5 kJ · mol^{-1}), where m_2/m_1 is less than one and the size ratio is greater than one (hence both the factors contribute to a larger activation energy). In the latter case, where the size ratio is less than one, while the mass ratio is greater than unity, the total activation energy is smaller (7.9 kJ · mol^{-1}).

The organic solutes studied in this work have a solute-to-solvent mass ratio which is greater than unity (except for benzene), and core size ratios less than one, except octafluorotoluene. Their activation energy values for diffusion are comparable to that of toluene in *n*-hexane.

Table III. Activation Energy, E_D, for Diffusion of Fluorobenzenes in *n*-Hexane

Compound	E_D (kJ · mol^{-1})
Benzene	8.55
o-Difluorobenzene	8.84
p-Difluorobenzene	8.80
1,2,4-Trifluorobenzene	8.33
1,2,3,5-Tetrafluorobenzene	8.80
1,2,4,5-Tetrafluorobenzene	8.72
Pentafluorobenzene	8.27
Hexafluorobenzene	8.42
Octafluorotoluene	8.43

On the basis of rough hard-sphere theory, the mutual diffusion coefficient D_{12} of rough hard-spherical molecules diffusing in a dense fluid is given [17] by

$$D_{12} = D_{\mathrm{E}} A_{12} (D/D_{\mathrm{E}})_{\mathrm{MD}} \tag{2}$$

where D_{E} is the Enskog smooth hard-sphere diffusion coefficient, A_{12} is the translational–rotational coupling constant, and $(D/D_{\mathrm{E}})_{\mathrm{MD}}$ is the correction to the Enskog theory to take into account correlated molecular motion.

For a dense hard-sphere mixture at temperature T, where the total number density is n, D_{E} is related to the low-density coefficient by the contact distribution function $g_{12}(\sigma)$:

$$D_{\mathrm{E}} = \frac{3(k_{\mathrm{B}}T)^{1/2}}{8n\sigma_{12}^2} \left(\frac{m_1 + m_2}{2\pi m_1 m_2} \right)^{1/2} \frac{1}{g_{12}(\sigma)} \tag{3}$$

where m_1 and m_2 are the molecular masses of the components, σ_{12} is the average core size, and k_{B} is the Boltzmann constant. $g_{12}(\sigma)$ is given by

$$g_{12}(\sigma) = [\sigma_1 g_{22}(\sigma) + \sigma_2 g_{11}(\sigma)]/2\sigma_{12} \tag{4}$$

where

$$g_{ii}(\sigma) = \frac{1}{1-\xi} + \frac{3y_i}{2(1-\xi)^2} + \frac{y_i^2}{2(1-\xi)^3} \tag{5}$$

ξ is equal to $\sum n_i \pi \sigma_i^3/6$ and $y_i = (\sigma_i \xi_j + \sigma_j \xi_i)/\sigma_j$.

Computed corrections to Enskog theory for different solute–solvent size and mass ratios have been given [18–20] for mixtures where solute is present in a trace amount. These values have been fitted by the following empirical expression [21], in which the first four terms reproduce the corrections to Enskog theory where the mass ratio and size ratio both equal unity [22].

$$\begin{aligned}(D/D_{\mathrm{E}})_{\mathrm{MD}} = {} & 0.58 + 7.08[0.6666 - (V_0/V)] \\ & - 20.2[0.6666 - (V_0/V)]^2 + 17.6[0.6666 - (V_0/V)]^3 \\ & + 0.29 \log(m_2/m_1) - 0.12[\log(m_2/m_1)]^2 - 0.42[(\sigma_2/\sigma_1) - 1] \\ & + 1.8(\sigma_2/\sigma_1) \log(m_2/m_1)[(V/V_0) - 1.6] \\ & - 0.42[(\sigma_2/\sigma_1) - 1] \log(m_2/m_1) - [(\sigma_2/\sigma_1) - 1]^2 \log(m_2/m_1)\end{aligned} \tag{6}$$

The $(D/D_{\mathrm{E}})_{\mathrm{MD}}$ in this work were calculated from Eq. (6), which gives a closer fit to the computed values than an earlier equation [20], especially

Table IV. Values of $(D/D_E)_{MD}$ and A_{12} for Fluorobenzenes in *n*-Hexane

	T(K)					
	233.2	253.2	273.2	298.2	313.2	333.2
Benzene						
$(D/D_E)_{MD}$	0.642	0.799	0.926	1.027	1.109	1.174
A_{12}	0.69	0.67	0.67	0.70	0.68	0.70
o-Difluorobenzene						
$(D/D_E)_{MD}$	0.659	0.833	0.975	1.088	1.191	1.273
A_{12}	0.67	0.67	0.68	0.70	0.67	0.69
p-Difluorobenzene						
$(D/D_E)_{MD}$	0.659	0.833	0.975	1.088	1.191	1.273
A_{12}	0.72	0.70	0.69	0.72	0.69	0.69
1,2,4-Trifluorobenzene						
$(D/D_E)_{MD}$	0.658	0.838	0.987	1.106	1.217	1.306
A_{12}	0.76	0.69	0.69	0.73	0.68	0.68
1,2,3,5-Tetrafluorobenzene						
$(D/D_E)_{MD}$	0.658	0.844	0.999	1.124	1.241	1.338
A_{12}	0.77	0.69	0.74	0.75	0.66	0.70
1,2,4,5-Tetrafluorobenzene						
$(D/D_E)_{MD}$	0.658	0.844	0.999	1.124	1.241	1.338
A_{12}	0.77	0.68	0.71	0.74	0.71	0.67
Pentafluorobenzene						
$(D/D_E)_{MD}$	0.651	0.843	1.004	1.134	1.258	1.360
A_{12}	0.83	0.73	0.69	0.70	0.68	0.67
Hexafluorobenzene						
$(D/D_E)_{MD}$	0.648	0.845	1.011	1.146	1.275	1.383
A_{12}	0.82	0.71	0.68	0.72	0.67	0.66
Octafluorotoluene						
$(D/D_E)_{MD}$	0.626	0.835	1.014	1.188	1.305	1.427
A_{12}	0.80	0.67	0.64	0.66	0.60	0.62

for mass and size ratios which differ significantly from unity, and are tabulated in Table IV.

Values of V/V_0 for *n*-hexane from 213.2 to 333.2 K were calculated from density values (API tables) and core sizes [23] over the range 223.2–333.2 K and extrapolated down to 213.2 K. The solute diameters were derived from viscosity data, and due to the lack of viscosity data over the entire temperature range, the solute–solvent diameter ratios were assumed to be constant at all temperatures. Tables V and VI list V/V_0 and σ for *n*-hexane as a function of temperature and $m_2/m_1, \sigma_2/\sigma_1$, and σ for solutes at 298.2 K.

The translational–rotational coupling factor A_{12} was calculated by fitting the experimental data to Eq. (2), with Eq. (6) for the correction to the Enskog values. The magnitude of A_{12} is a measure of the roughness of the molecules (or the departure of the molecule from a spherical shape). The values of A_{12} over the temperature range 233.2–333.2 K for these organic solutes generally lie within the range 0.67 to 0.72. Although the mass ratio of the solutes ranges from 0.9 to 2.74 and the size ratio varies from 0.9 to 1.02, the A_{12} values are very close to the A_{11} value of *n*-hexane derived from self-diffusion data. The A_{12} value is roughly temperature independent for benzene and *o*-and *p*-difluorobenzene but shows a slightly irregular variation with temperature for the other solutes. The average of the 54 A_{12} values for the nine solutes at six temperatures is 0.70 ± 0.04, which is as expected for systems of rough aspherical molecules [24]. When D_{12} was calculated for these solutes with $A = 0.72$, equal to the value of A_{11} for *n*-hexane at 298.2 K, the absolute average percentage deviation of the 54 data points was 5.5%. Only five points have a deviation greater than 10%, of which four are for octafluorotoluene and the other corresponds to pentafluorobenzene at 233.2 K.

In spite of the fact that (i) the experimental uncertainty of the measurements is 2.5%, (ii) the computed correction is made on the assumption that the solute–solvent diameter ratios are temperature independent, (iii) there is uncertainty in the extrapolated or interpolated core size of *n*-hexane, (iv) the molecules depart from spherical shape to varying

Table V. V/V_0 and Core Sizes of *n*-Hexane as a Function of Temperature

	T(K)						
	213.2	233.2	253.2	273.2	293.2	313.2	333.2
V/V_0	1.4510	1.5090	1.5685	1.6255	1.6872	1.7540	1.8188
σ (nm)	0.5673	0.5733	0.5706	0.5683	0.5660	0.5647	0.5635

Table VI. Solute-to-Solvent Mass and Size Ratios and Core Sizes of Solutes at 298.2 K

Compound	m_2/m_1	σ_2/σ_1	σ (nm)
n-Hexane	1.00	1.00	0.566
Toluene	1.07	0.97	0.549
Acetonitrile	0.50	0.72	0.409
Benzene	0.91	0.90	0.509
o-Difluorobenzene	1.32	0.92	0.521
p-Difluorobenzene	1.32	0.92	0.521
1,2,4-Trifluorobenzene	1.53	0.94	0.532
1,2,3,5-Tetrafluorobenzene	1.74	0.95	0.538
1,2,4,5-Tetrafluorobenzene	1.74	0.95	0.538
Pentafluorobenzene	1.95	0.97	0.549
Hexafluorobenzene	2.16	0.98	0.555
Octafluorotoluene	2.74	1.02	0.577

extents, and (v) there is uncertainty in the computed corrections to Enskog theory, the near-constancy of A_{12} is remarkable. Although the molecules are nonspherical in shape, the data can be reproduced satisfactorily on the basis of the rough hard-sphere model with the translational–rotational coupling factor equal to that of the solvent.

6. CONCLUSIONS

Mutual diffusion coefficients for fluorinated benzenes diffusing in *n*-hexane are reported at temperatures from 213.2 to 333.2 K with an estimated uncertainty of 2.5%. An Arrhenius-type equation gives a reasonable fit to the temperature dependence of D_{12} for each mixture. The data can be reproduced satisfactorily on the basis of the rough hard-sphere theory with a translational–rotational coupling factor of 0.70 ± 0.04, which is close to the A_{11} value for the solvent.

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