

Tracer Diffusion of Organic Solutes in n-Hexane at Pressures up to 400 MPa

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Tracer diffusion coefficient measurements in n-hexane have been made using a high-pressure diaphragm cell for [¹⁴C]benzene, [¹⁴C]toluene, [*G*-³H]benzo[*a*]pyrene, [¹⁴C]carbon disulphide and [¹⁴C]acetonitrile at 298.2 K and at pressures up to 400 MPa. The results, which have an estimated accuracy of $\pm 2\%$ up to 240 MPa and $\pm 4\%$ at the higher pressures, have been satisfactorily interpreted on the basis of the rough hard-sphere model.

The van der Waals picture of a dense fluid, which is equivalent to the hard-sphere model for transport properties, has proved a very satisfactory basis for the interpretation of transport coefficient data of single-component systems of atoms,^{1,2} pseudo-spherical molecules^{1,3,4} and even non-spherical molecules,^{5,6} providing that account is taken of the possibility of changes in angular momentum as well as in linear momentum on collision.⁷ One serious disadvantage of this model is that it predicts a phase transition at a density significantly less than the density at which a real liquid solidifies at any given temperature, and this limits the applicability of the model to a fraction of the normal liquid range. However, it has been shown⁸ that the predictions of this model provide a basis for the successful correlation of experimental transport coefficient data over the whole liquid range.

It is therefore of interest to determine whether transport coefficient data for mixtures can also be satisfactorily interpreted on the basis of the rough hard-sphere model. A previous application⁹ of this model to mutual diffusion in binary liquid mixtures showed that for nearly ideal solutions the calculated diffusion coefficient was in excellent agreement with experiment. However, the calculations were based on the assumption that the mass and size ratios were equal to unity and only data at atmospheric pressure were considered. In order to make a rigorous test of the theory it is necessary to have accurate experimental data over a wide range of experimental conditions. In this paper we report measurements on the tracer diffusion coefficient for different organic solutes diffusing in n-hexane at 298.2 K and at pressures up to 400 MPa using a high-pressure diaphragm cell. Details of the experimental method have been given earlier¹⁰ and the only modifications were to the pressure vessel to enable the pressure range to be extended above 240 MPa and to the cell, where a new top dome section was made to accommodate the greater changes in volume. The experimental results are used to estimate the activation volume and to examine the Stokes-Einstein relationship. For a comparison with the predictions of the rough hard-sphere theory, the data are reduced in terms of the self-diffusion coefficient data of the solvent at the same density obtained by the n.m.r. spin-echo technique.¹¹

EXPERIMENTAL

DIFFUSION MEASUREMENTS

The high-pressure diaphragm cells, the experimental procedures for their use and the method of calculation of the diffusion coefficient have been described previously.^{10,12} The only modification necessary to extend the pressure range from the maximum of 240 to 400 MPa was the replacement of the pressure vessel closure by a new closure with a higher tensile strength manufactured from a martensitic chrome-nickel steel, Bohler Antinit AS17N4, conforming to AISI 17-4PH. The diffusion experiments were made using [¹⁴C]labelled benzene, [¹⁴C]labelled toluene, [*G*-³H]benzo[*a*]pyrene, [¹⁴C]labelled carbon disulphide and [¹⁴C]labelled acetonitrile from the Radiochemical Centre, Amersham. All experiments were carried out using the solvent-filled diaphragm technique¹³ with the tracer material added to the top compartment of the diffusion cell. Corrections were made to the measured concentrations for the bulk-flow which occurs at the end of each pressure experiment.¹⁰

The compressibility data needed to calculate the cell compartment volumes and bulk-flow corrections were obtained from densities given in the literature.¹⁴

MATERIALS AND COUNTING PROCEDURE

Spectroscopic grade n-hexane was supplied by Merck. Measured diffusion coefficients, in a glass diaphragm cell at atmospheric pressure for a trace of benzene in n-hexane which had been carefully dried, fractionally distilled and the middle fraction taken, agreed to within the estimated uncertainty with measured coefficients obtained using the undistilled solvent. Counting procedures and equipment have been fully described elsewhere.¹³ For n-hexane, the scintillator solution consisted of 4 g dm⁻³ PPO and 0.4 g dm⁻³ POPOP in toluene and a ratio of 1 part of active liquid to 10 parts of scintillator solution was used.

RESULTS AND DISCUSSION

The tracer diffusion results obtained with the diaphragm cell are given in table 1, together with densities, calculated from the secant bulk modulus,¹⁴ which have an estimated accuracy of 0.2%. The errors inherent in the diffusion coefficient measurement have been extensively discussed and it is estimated that the results have an accuracy of $\pm 2\%$ at pressures up to 240 MPa and $\pm 4\%$ at higher pressures.

The atmospheric pressure diffusion coefficients for benzene in n-hexane agree to within 1% with the all-glass diaphragm cell measurement¹⁵ of $4.747 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and are in good agreement with limiting mutual diffusion coefficient values of $4.758 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ¹⁶ and $4.723 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,¹⁷ obtained using a diffusimeter.

The measured tracer diffusion coefficient for toluene in n-hexane at atmospheric pressure agrees closely with the all-glass diaphragm cell value¹⁸ of $4.335 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Tracer diffusion coefficients in n-hexane for benzo[*a*]pyrene, carbon disulphide and acetonitrile measured in the high-pressure cell agreed to within 1.5% with measurements in an all-glass cell.

The effect of increased pressure on the tracer diffusion coefficients is illustrated in fig. 1. It is clear that the variation of $\log D$ with pressure is not linear. Although there is both theoretical evidence¹⁹ and experimental evidence²⁰ to show that the activation model is not valid, the dependence of diffusion-coefficient data on pressure is frequently represented in terms of an activation volume ΔV_D defined by

$$\Delta V_D = -RT \left(\frac{\partial \ln D}{\partial p} \right)_T. \quad (1)$$

TABLE 1.—TRACER DIFFUSION COEFFICIENTS OF ORGANIC SOLUTES IN n-HEXANE AT 298.2 K

solute	p/MPa	$\rho(\text{n-hexane})/\text{kg m}^{-3}$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$
$[^{14}\text{C}]$ benzene	0.101	655.0	4.71 ₁ , 4.76 ₀
	18.7	671.4	4.12 ₃
	44.6	691.7	3.43 ₄
	88.1	712.9	2.81 ₂
	124.3	732.7	2.20 ₂
	160.3	746.4	1.83 ₁
	198.0	757.2	1.54 ₆
	217.5	765.2	1.38 ₈
	282.4	783.0	1.10 ₄
	292.1	784.4	1.07 ₀
	369.3	803.4	0.75 ₁
$[^{14}\text{C}]$ toluene	0.101	655.0	4.37 ₇
	41.1	688.8	3.26 ₂
	78.1	710.8	2.63 ₀
	124.1	732.7	2.03 ₄
	191.6	757.0	1.49 ₇
	244.9	772.9	1.10 ₁
	294.2	786.3	0.93 ₅
	375.0	805.7	0.70 ₀
$[G-^3\text{H}]$ benzo[<i>a</i>]pyrene	0.101	655.0	2.68 ₄ , 2.64 ₆ ^a
	78.2	710.8	1.56 ₈
	129.3	735.1	1.19 ₄
	217.3	765.0	0.80 ₆
	291.1	785.4	0.57 ₅
	369.8	803.5	0.41 ₆
$[^{14}\text{C}]$ carbon disulphide	0.101	655.0	5.84 ₀ , 5.92 ₈
	0.101	655.0	5.96 ₂ , 5.90 ₃ ^a
	40.0	687.8	4.36 ₄
	102.6	723.4	3.23 ₄
	163.4	748.0	2.43 ₉
	221.6	767.6	1.91 ₈
	261.1	779.3	1.66 ₉
	301.2	789.4	1.33 ₅
	324.7	795.0	1.30 ₉
	384.0	807.4	1.06 ₅
$[^{14}\text{C}]$ acetonitrile	0.101	655.0	6.10, 6.13 ^a
	39.1	686.4	4.50 ₃
	85.9	715.3	3.80 ₂
	102.2	723.2	3.11 ₄
	146.0	741.4	2.70 ₅
	218.8	766.8	2.07 ₃
	385.6	807.6	1.08 ₃

^a Glass diaphragm cell measurements.

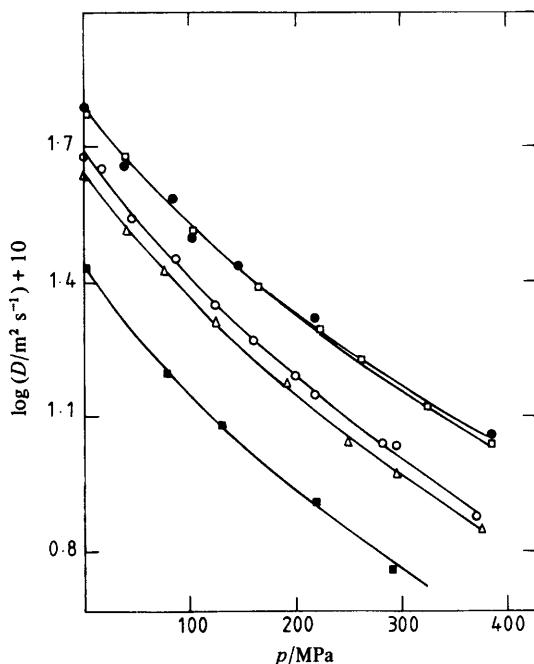


FIG. 1.—Effect of elevated pressure on tracer diffusion coefficients at 298.2 K. Key to tracers: ○, $[^{14}\text{C}]$ benzene; △, $[^{14}\text{C}]$ toluene; ■, $[G-^3\text{H}]$ benzo[*a*]pyrene; ●, $[^{14}\text{C}]$ acetonitrile; □, $[^{14}\text{C}]$ carbon disulphide.

Activation volumes are given to within $0.4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for the aromatic hydrocarbons diffusing in n-hexane by the equation

$$10^6 \Delta V_D = 17.4 - 0.04p + 0.00004p^2 \quad (2)$$

and for carbon disulphide and acetonitrile diffusing in n-hexane by the equation

$$10^6 \Delta V_D = 16.3 - 0.04p + 0.00004p^2 \quad (3)$$

where p is in MPa. This difference in the activation volumes for these two groups of tracers arises from the smaller sizes of acetonitrile and carbon disulphide.

In general, the magnitude of tracer diffusion coefficients depends upon the relative molecular masses, the relative sizes and shapes, and the strengths of the molecular interactions. Fig. 2 shows that the pressure dependence of the present tracer diffusion-coefficient data is practically identical for the different aromatic hydrocarbons diffusing in n-hexane and is in very close agreement with the pressure dependence of the self-diffusion coefficient of n-hexane at 298.2 K determined from n.m.r. spin-echo measurements.¹¹ This is an interesting and unexpected result since the tracer molecules vary significantly in mass, size and shape from benzene and n-hexane to the five fused-ring molecule of benzo[*a*]pyrene, and their molecular interactions with n-hexane will differ also. The tracer diffusion coefficient for carbon disulphide in n-hexane shows the same pressure dependence as that for acetonitrile in n-hexane, but the pressure dependence is significantly lower than for trace hydrocarbons in n-hexane. The difference increases to 17% at 400 MPa.

These differences can be interpreted on a molecular basis by consideration of the

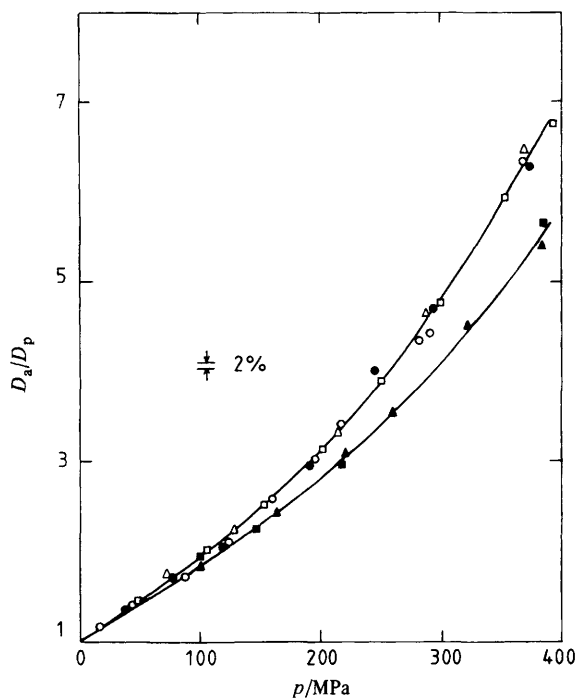


FIG. 2.—Effect of elevated pressure on the ratio of the tracer diffusion coefficients at atmospheric pressure and at pressure p , compared with the corresponding ratio of the self-diffusion coefficient of n-hexane at 298.2 K. \square . Key: \circ , $[^{14}\text{C}]$ benzene; \bullet , $[^{14}\text{C}]$ toluene; \triangle , $[G-^3\text{H}]$ benzo[a]pyrene; \blacktriangle , $[^{14}\text{C}]$ carbon disulphide, \blacksquare , $[^{14}\text{C}]$ acetonitrile.

results obtained from molecular-dynamics studies on the effects of varying molecular parameters separately on tracer diffusion coefficients. Such calculations have been carried out at different densities for hard-sphere systems²¹ where the single test particle has a mass and size less than that of the solvent.

On the basis of the rough hard-sphere model, the binary diffusion coefficient for a dense fluid mixture is given by

$$D_{12} = \frac{3(kT)^{\frac{1}{2}}}{8n\sigma_{12}^2} \left(\frac{m_1 + m_2}{2\pi m_1 m_2} \right)^{\frac{1}{2}} \frac{A_{12}}{g_{12}(\sigma)} \left(\frac{D}{D_E} \right)_{\text{MD}} \quad (4)$$

where n is the total number density, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ for spheres of diameter σ , m_1 , m_2 are the molecular masses and $(D/D_E)_{\text{MD}}$ is the computed correction²¹ to the Enskog value. A_{12} is the translation-rotation coupling constant and $g_{12}(\sigma)$ is the unlike radial distribution function at contact which is given in terms of the like radial distribution functions by²²

$$g_{12}(\sigma) = [\sigma_1 g_{22}(\sigma) + \sigma_2 g_{11}(\sigma)] / 2\sigma_{12} \quad (5)$$

where $g_{ii}(\sigma)$ is given by

$$g_{ii}(\sigma) = \frac{1}{1-x} + \frac{3y_i}{2(1-x)^2} + \frac{y_i^2}{2(1-x)^3} \quad (6)$$

$x = x_1 + x_2$, with x_i equal to $\pi n_i \sigma_i^3 / 6$, and $y_i = (\sigma_i x_j + \sigma_j x_i) / \sigma_j$.

When component 2 is present in trace concentration the expression reduces to

$$g_{12}(\sigma) = \left[1 + \frac{(\sigma_2 - 2\sigma_1)x_1}{(\sigma_2 + \sigma_1)} + \frac{(2\sigma_1 - \sigma_2)(\sigma_1 - \sigma_2)x_1^2}{2\sigma_1(\sigma_1 + \sigma_2)} \right] / (1 - x_1)^3. \quad (7)$$

This expression differs significantly from the approximate result of Lebowitz²³ which is seriously in error at densities approaching the normal liquid densities as shown by a comparison with molecular dynamics results. The Thorne equation²⁴ for $g_{12}(\sigma)$ gives values significantly lower than computed values even at densities corresponding to critical densities.

Computed corrections to Enskog theory for different solute-solvent mass and size ratios are given^{21,25} at V/V_0 values of 3.0, 1.6 and 1.5, where $V_0 = N\sigma^3/\sqrt{2}$. For comparison, V/V_0 for n-hexane at atmospheric pressure is *ca.* 1.7. Core sizes required for calculation of binary diffusion coefficients were derived from self-diffusion-coefficient data using the expression given earlier²⁶ for a hard-sphere system but modified for rough hard spheres:

$$10^9 D = \frac{2.527A}{V_0^{1/3}} \left(\frac{RT}{M} \right)^{1/2} (V - 1.384 V_0) \quad (8)$$

where A is the translation-rotation coupling constant for the single-component system.

Values of A , V_0 and σ for n-hexane, benzene, carbon disulphide and acetonitrile derived using eqn (8) from self-diffusion-coefficient data^{11, 27, 28} at 298 K are given in table 2. For acetonitrile, A is significantly smaller than the lower limit calculated for rough hard spheres²⁹ but this is not unexpected for a real molecule which is non-spherical and has an asymmetric mass distribution.

TABLE 2.—VALUES OF A , V_0 AND σ FROM SELF-DIFFUSION-COEFFICIENT DATA AT 298.2 K

liquid	A	$V_0/10^{-6} \text{ m}^3 \text{ mol}^{-1}$	σ/nm
n-hexane	0.72	77.3	0.566
benzene	0.67	56.8	0.511
carbon disulphide	0.67	33.4	0.428
acetonitrile	0.55	29.1	0.409

These parameters can be used in eqn (4) for direct calculation of the limiting intradiffusion coefficients D_2° since most theories agree that these are identical to limiting mutual diffusion coefficients D_{12}^∞ for $x_1 \rightarrow 1$. However, for a comparison of the pressure dependence of the tracer diffusion coefficients predicted on the basis of the hard-sphere theory with the experimental results, it is convenient to reduce the data in terms of the self-diffusion coefficient of the pure solvent $D_1(1)$ at the same density. This reduces the uncertainties associated with the extrapolation of the computer corrections to Enskog theory to infinite particle systems. The variation of the ratio $D_2^\circ/D_1(1)$ with mass ratio and size ratio is given for rough hard spheres by the equation

$$\frac{D_2^\circ}{D_1(1)} = \frac{D_{12}^\infty}{D_1(1)} = 2\sqrt{2} \frac{(m_1/m_2 + 1)^{1/2}}{(\sigma_2/\sigma_1 + 1)^2} \frac{g_{11}(\sigma)}{g_{12}(\sigma)} \frac{A_{12}}{A_{11}} \frac{(D/D_E)_{12}}{(D/D_E)_{11}} \quad (9)$$

with $g_{12}(\sigma)$ given by eqn (5).

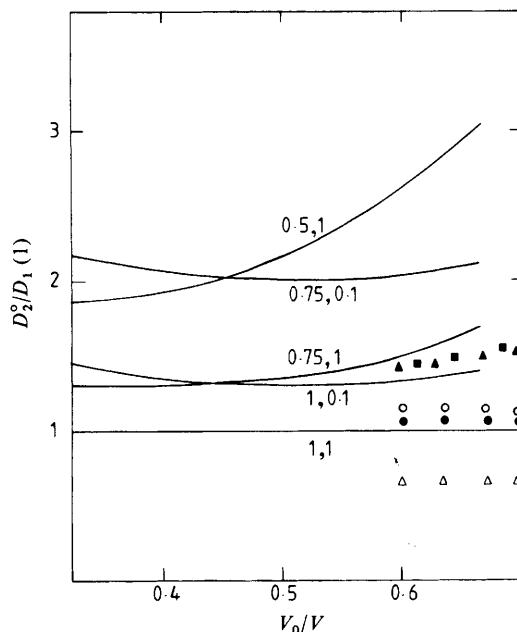


FIG. 3.—Comparison of experimental ratio of the limiting tracer diffusion coefficient to the self-diffusion coefficient of the solvent at different reduced volumes with calculated values for the rough hard-sphere model for different tracer:solvent size ratios, mass ratios as given. Key as for fig. 2.

The variation of $D_2^0/D_1(1)$ with V_0/V is illustrated in fig. 3 on the assumption that $A_{12} = A_{11}$, at fixed m_2/m_1 and σ_2/σ_1 values for $V_0/V > 0.3$. The shape of the curves in this region has been determined from curves which include the low-density intercepts. For binary mixtures where the size ratio is approximately one, the ratio of tracer diffusion coefficient to self-diffusion coefficient of the solvent is predicted to be pressure independent for densities above twice the critical density. Where the solute molecule is appreciably smaller than the solvent molecule, the pressure dependence of $D_2^0/D_1(1)$ becomes more marked, the ratio increasing on going to higher pressures. At present there are no published computer data for diffusion coefficients of hard-sphere systems where the solute is larger than the solvent. However, it is expected that $D_2^0/D_1(1)$ will show little pressure dependence until σ_2/σ_1 becomes much greater than one, when a decrease in $D_2^0/D_1(1)$ with increasing pressure is predicted. For a given size ratio, the change in solute:solvent mass ratio from 1 to 0.1 leads to an increase in $D_2^0/D_1(1)$ of 35% at $\sigma_2/\sigma_1 = 1$, increasing to *ca.* 55% at $\sigma_2/\sigma_1 = 0.5$.

Values of $D_2^0/D_1(1)$ calculated from the present measurements are included in fig. 3. Although these molecules are not spherical in shape it is remarkable how closely these results agree with the hard-sphere predictions. The ratio for the aromatic hydrocarbons diffusing in n-hexane shows no pressure dependence. $D_2^0/D_1(1)$ with benzene as tracer is higher than that for toluene tracer as expected from consideration of the relative values of tracer:solvent mass and size ratios given in table 3. As $\sigma_2/\sigma_1 < 1$, $D_2^0/D_1(1)$ is predicted by the model to be a few percent greater than one, in agreement with experiment. For benzo[a]pyrene the estimated size is significantly greater than that of n-hexane. Extrapolation of the values of $D_2^0/D_1(1)$ for a mass ratio of unity at size ratios of 0.5, 0.75 and 1.0 gives $D_2^0/D_1(1)$ between 0.7 and 0.8 at

TABLE 3.—TRACER : n-HEXANE MASS AND SIZE RATIOS AT 298.2 K

tracer	m_2/m_1	σ_2/σ_1
[¹⁴ C]benzene	0.93	0.905
[¹⁴ C]toluene	1.09	(0.94) ^a
[¹⁴ C]acetonitrile	0.50	0.723
[¹⁴ C]carbon disulphide	0.93	0.756
[G- ³ H]benzo[a]pyrene	2.92	(1.23) ^a

^a Estimated.

$V_0/V > 0.6$ for this estimated size ratio. The predicted ratio will be further reduced for a much heavier trace molecule, in close agreement with the experimental result.

The experimental $D_2^0/D_1(1)$ ratios for carbon disulphide lie a few percent below the line for $\sigma_2/\sigma_1 = 0.75$ and a mass ratio of unity as expected since σ_2/σ_1 for this system is marginally greater than 0.75. Acetonitrile has half the molecular mass of n-hexane and $\sigma_2/\sigma_1 < 0.75$, and yet the experimental points lie close to those of carbon disulphide. This suggests that whereas the assumption that $A_{12} = A_{11}$ is valid for the other systems, for acetonitrile + n-hexane the unlike translation-rotation coupling constant A_{12} is *ca.* 20% less than A_{11} . The conclusion is in accord with the values derived for A_{11} and listed in table 2, which differ by only a few percent for benzene, carbon disulphide and n-hexane but are on average *ca.* 25% greater than the value for acetonitrile.

These results can form the basis of an accurate predictive method for tracer diffusion coefficients under elevated pressure. If the self-diffusion coefficient of the solvent is accurately known over the pressure range it is only necessary to measure the tracer diffusion coefficient at atmospheric pressure. From the value of $D_2^0/D_1(1)$ and approximate knowledge of the ratios σ_2/σ_1 and m_2/m_1 , the density dependence of $D_2^0/D_1(1)$ can be drawn and D_2^0 calculated for elevated pressures.

The molecules considered here are neither hard nor spherical and the inference is that non-spherical shape and realistic forms of the intermolecular potential-energy function will affect the calculated $D_1(1)$ and D_2^0 coefficients to approximately the same extent, so that the general picture produced in fig. 3 of the effects of differences in molecular mass and size ratios on $D_2^0/D_1(1)$ is essentially unchanged. Confirmation of this must await the results of computer calculations at different densities and temperatures for molecules with different forms of intermolecular potential-energy function. Results that have been obtained³⁰ for atoms interacting with a Lennard-Jones (12-6) potential-energy function at a reduced temperature of one confirm that variations in the size ratio at a constant mass ratio produce a significantly greater change in $D_2^0/D_1(1)$ than corresponding changes in mass ratio for a constant size ratio. Although the computed results are given for a finite (108) particle system, for atoms of equal size $D_2^0/D_1(1)$ has the value of 1.14 for $m_2/m_1 = 0.5$ and 0.83 for $m_2/m_1 = 2.0$ in close agreement with the hard-sphere predictions. For atoms of equal mass with $\sigma_2/\sigma_1 = 0.5$, $D_2^0/D_1(1)$ is 1.79, which at the equivalent V_0/V value of 0.55 is lower than the hard-sphere results. Further computations are necessary and experimental measurements should be made for systems where the tracer and solvent have widely different sizes. For neon or acetonitrile in octamethylcyclotetrasiloxane at 323 K for example the ratio of tracer diffusion coefficient to self-diffusion coefficient of the liquid solvent should be greater than three and this ratio can be expected to increase rapidly

with increase in pressure. Such measurements would provide a critical test of the assumption of the equivalence of A_{11} and A_{12} .

A final point concerning the present measurements is that they can be used in conjunction with recent accurate measurements³¹ of the viscosity coefficient of n-hexane at 298.2 K to test the validity of the Stokes-Einstein equation

$$D_2^0 = \frac{kT}{a\pi\eta r} \quad (10)$$

where D_2^0 is the limiting diffusion coefficient at zero concentration of spheres of radius r moving in a hydrodynamic continuum of viscosity coefficient η . a is a constant and k is Boltzmann's constant.

At the same temperature it follows that

$$\frac{D_a}{D_p} = \frac{\eta_p}{\eta_a} \quad (11)$$

where subscripts a or p denote the value of the limiting tracer diffusion coefficient or solvent viscosity at atmospheric pressure or elevated pressure. This relationship is tested in fig. 4. The ratios are identical only at very low pressures. A similar result has been found for benzene and cyclohexane from self-diffusion-coefficient data. However, a comparison of fig. 4 and 2 indicates that $D_a/D_p \rightarrow \eta_p/\eta_a$ as the size of the solute particle increases. This is in general agreement with the conclusion of a recent re-examination of Stokes' Law.²⁹

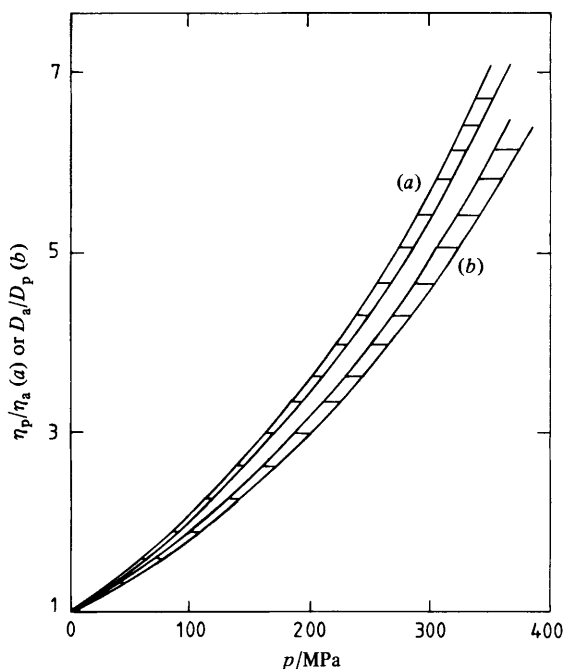


FIG. 4.—Test of the Stokes-Einstein relationship. The shaded region indicates the possible range of values for the ratios of viscosity coefficients of n-hexane and tracer diffusion coefficients for the hydrocarbons in n-hexane at 298.2 K.

CONCLUSION

Tracer diffusion-coefficient measurements for [^{14}C]benzene, [^{14}C]toluene, [$G-^3\text{H}$]benzo[*a*]pyrene, [^{14}C]carbon disulphide, and [^{14}C]acetonitrile in n-hexane at 298.2 K at pressures up to 400 MPa have been interpreted very satisfactorily on the basis of the rough hard-sphere model.

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