

Diffusion of Pseudo-planar Molecules: An Experimental Evaluation of the Molecular Effects on Diffusion

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Limiting mutual-diffusion coefficients of non-associated pseudo-planar molecules, ranging from benzene to anthracene, in various solvents have been measured at 298.2 K using the chromatographic peak-broadening method. For the non-associated solutes studied, there exists a linear relationship between the reciprocal of the diffusion coefficients and the molecular volume of the solutes. The diffusivities are found to be insensitive to the mass and dipole moment of the solute molecules. The data of the pseudo-planar molecules are compared with those of the pseudo-spherical solutes reported in the literature. The effects of molecular shape on diffusion are discussed.

Transport properties of dense fluids have been understood basically in terms of the van der Waals (VDW) picture of condensed matter. According to that model, the structural arrangements and motions of molecules in a liquid are determined primarily by the local packing and steric effects produced by the short-range repulsive intermolecular forces. Attractive forces, dipole–dipole interactions, and other slowly varying interactions play only a minor role. Details of the VDW picture have been reviewed by Chandler *et al.*¹

There has been a continuous interest^{2–28} in the use of the rough-hard-sphere (RHS) theory^{29,30} for the interpretation of diffusion data. Based on the VDW picture, the RHS theory predicts mutual diffusion coefficients by the relation:^{23,31,32}

$$D_{12} = \frac{3(kT)^{1/2}}{2n_2(\sigma_1 + \sigma_2)^2} \left(\frac{1}{2\pi\mu} \right)^{1/2} \frac{A_{12}}{g_{12}} \left(\frac{D_{\text{SHS}}}{D_E} \right) \quad (1)$$

Where, D_{12} is the limiting mutual-diffusion coefficients, n_2 represents the number density of the solvent, μ is the reduced mass of solute and solvent molecules, σ_1 and σ_2 refer to the molecular diameters of solute and solvent, respectively, A_{12} is the translation–rotation coupling constant, D_{SHS}/D_E represents the computed correction to the Enskog theory to take account of the correlated molecular motions, and g_{12} is the unlike radial-distribution function at contact.

The RHS theory, however, has not been tested critically for its range of applicability. It appears in particular that still very little is known about the translation–rotation coupling constant, a parameter closely related to the shape of the colliding particles,²⁹ in that theory.

In this paper we report limiting mutual-diffusion coefficients of aromatic molecules ranging from benzene to anthracene in ethanol, acetone and *n*-tetradecane at 298.2 K. The solutes are all pseudo-planar in shape, and the solvents are selected to represent protic, aprotic and hydrocarbon solvents. The purpose of this work is to investigate the effect of molecular shape on diffusion by comparing the present data with those of the pseudo-spherical solute molecules reported elsewhere. The present experiment is also designed to probe information concerning the effects of molecular mass, size and dipole moment on diffusion. Moreover, the results of the non-associated solute molecules here will provide a basis³³ for the study of the effects of solute association on diffusion.

Experimental

The diffusion measurements were made using the chromatographic peak-broadening method,³⁴ known also as the

Taylor dispersion technique. In this method, a small sample of a dilute solution is injected into a stream of solvent in a capillary tube. Taylor³⁵ has shown that for a laminar flow the combination of flow and diffusion results in a Gaussian distribution of solute along the tube. The diffusion coefficient for liquids can be determined from the equation³⁶

$$D_{12} = 0.2310R^2t_r/(W_{1/2})^2$$

where D_{12} is the mutual-diffusion coefficient, R is the internal radius of the diffusion tube, t_r is the residence time of the solute in the tube, and $W_{1/2}$ is the width at half-height of the eluted peak.

The experimental setup and procedure for measurements of mutual-diffusion coefficients have been described previously.^{14,15} Briefly, the diffusion tube was an 85.7 m length of 304 stainless-steel tube of 1.59 mm o.d. and 0.98 mm i.d. The capillary tubing was coiled in a 40 cm diameter circle and placed in a constant-temperature bath which was controlled to 298.15 ± 0.02 K. A 20–50 mm³ sample was injected through a septum injector into the solvent stream. To ensure laminar flow, the solvent flow rate was adjusted so that the constant volume flow was only between 0.1 and 0.2 cm³ min^{−1}. At the end of the diffusion tube, the solute dispersion peak was detected with a Waters differential refractometer, model R401, with output to a chart recorder. The temperature of the refractometer cell was controlled by circulating water from the constant-temperature bath.

In this experiment, the solvents acetone (99.5%+, BDH), ethanol (99.5%+, Ajax), and *n*-tetradecane (99%+, TCI) were used as received. The solute chlorobenzene (98%, BDH) was purified by fractional distillation; benzene (99.9%, Aldrich), toluene (99.5%, E. Merck), ethylbenzene (99%+, BDH), naphthalene (99%+, BDH), 1,2,4-trichlorobenzene (99%+, Aldrich), *n*-propylbenzene (99%, E. Merck), biphenyl (99%+, Koch-Light) and anthracene (99.9%, Aldrich) were used without further purification.

Results and Discussion

The mutual-diffusion coefficients as determined by the chromatographic peak-broadening apparatus are summarized in Table 1. The reported values are the averages of three or more diffusion measurements. The uncertainty listed is the average absolute error.

The limiting mutual-diffusion coefficient of benzene in ethanol has been reported by Babb and co-workers.⁴⁴ Our value of 1.79×10^{-9} m² s^{−1} at 298.15 K as shown in Table 1

Table 1 Limiting mutual-diffusion coefficients ($D_{12}/10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 298.2 K

	VDW volume/ \AA^3 ^a	D_{12}		
		acetone	ethanol	<i>n</i> -tetradecane
pseudo-planar solute				
benzene	81.10	4.07 ± 0.04	1.79 ± 0.01	1.18 ± 0.01
chlorobenzene	97.17	3.71 ± 0.03	1.61 ± 0.01	1.06 ± 0.01
toluene	97.63	3.75 ± 0.03	1.62 ± 0.02	1.07 ± 0.01
ethylbenzene	113.8	3.45 ± 0.02	1.45 ± 0.01	0.953 ± 0.008
naphthalene	125.4	3.25 ± 0.03	1.32 ± 0.01	0.889 ± 0.007
1,2,4-trichlorobenzene	129.3	3.13 ± 0.03	1.28 ± 0.01	0.832 ± 0.008
propylbenzene	130.0	3.24 ± 0.03	1.32 ± 0.02	0.871 ± 0.008
biphenyl	152.4	2.89 ± 0.03	1.19 ± 0.01	0.792 ± 0.009
anthracene	169.7	2.85 ± 0.03	1.04 ± 0.01	—
pseudo-spherical solute ^b				
carbon tetrachloride	88.80	3.63 ± 0.03	1.50 ^c	0.897 ± 0.006
tetramethyltin	114.9	3.38 ± 0.03	1.25	0.812 ± 0.007
tetraethylmethane	156.1	3.11 ± 0.02	—	0.654 ± 0.006
tetraethyltin	179.6	2.92 ± 0.04	0.950	0.608 ± 0.003
tetrapropyltin	244.3	2.36 ± 0.03	—	0.475 ± 0.006
tetrabutyltin	309.0	2.00 ± 0.02	0.604	0.388 ± 0.005

^a The values are averages from ref. 37–40. ^b From ref. 41 and 42 except where noted otherwise. ^c From ref. 43.

agrees satisfactorily with their value of $1.81 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ measured at 298.30 K. When correction for temperature difference is taken into account, the agreement is estimated to be within our experimental error. The accuracy and reproducibility of data here are consistent with those reported in the literature^{11–16,22,24,34,36,41,42,45–49} for measurements using the same technique.

Diffusion coefficients of pseudo-spherical solutes in various solvents have been reported.^{41,42} Table 1 includes the data for solvents acetone, ethanol and *n*-tetradecane at 298.2 K. Also shown in the table are values of the VDW volume of the solute molecules, which are calculated from group increments given in the literature.^{37–40} When the reciprocal of the diffusion coefficients ($1/D_{12}$) is plotted against the molecular volume of the solutes, a fairly linear relationship is observed for all data of pseudo-planar and pseudo-spherical solutes in acetone. This correlation is found, however, only for solutes with similar shape in ethanol and *n*-tetradecane. It should be noted that the linear relationship exists despite the differences in mass and dipole moment of the various solute molecules. The effects of mass and dipole moment on diffusion are indeed small or insignificant as compared with the effect of molecular size found in this study. It is of particular interest to compare the data between chlorobenzene and toluene. These two solute molecules are of about the same size and shape. The close resemblance in size between a chloride group and methyl group has already been discussed.³¹ The two solutes are nevertheless different in molecular mass by 20%. The dipole moments for toluene and chlorobenzene are 0.36 and 1.69 D, respectively.⁵⁰ Table 1 shows that the diffusion coefficients of toluene and chlorobenzene are approximately equal in each solvent. This indicates that diffusivities are insensitive to the mass and dipole moment of the solute molecules. Similar conclusions have also been reached in our previous studies on the diffusion of di-substituted benzene¹⁴ and pseudo-spherical solutes.¹⁵ This insensitivity of diffusion to solute dipole moment further justifies the basic assumption made in the RHS theory, *i.e.* attractive and other forces which vary slowly in space are unimportant in affecting the molecular motions in liquids.

Another comparison is available between 1,2,4-trichlorobenzene and propylbenzene. These two aromatic solutes are also similar in size. Table 1 shows that a 50% increase in molecular mass yields only a small decrease in the diffusion coefficients (the maximum being 4.5%) from propylbenzene

to 1,2,4-trichlorobenzene. Note, however, that the two molecules are slightly different in their pseudo-planar shape.

Fig. 1–3 show the variation of $1/D_{12}$ with solute volume for the solvent systems acetone, ethanol and *n*-tetradecane. The linear relationships between $1/D_{12}$ and the VDW volume of solutes found in this work can be used to examine the RHS theory. The translation–rotation coupling constant A_{12} in eqn. (1) has been suggested to depend only on the shape of the colliding particles.²⁹ For solutes with the same shape diffusing in a given solvent at constant temperature, eqn. (1) can be simplified to

$$D_{12} \propto \frac{(D_{\text{SHS}}/D_{\text{E}})}{(\sigma_1 + \sigma_2)^2 g_{12} \mu^{1/2}} \quad (2)$$

Eqn. (2) is also applicable for solutes with different shapes if the effect of shape is insignificant.

The computed correction to the Enskog theory, $D_{\text{SHS}}/D_{\text{E}}$, is a function³² only of the mass and size of solutes in a particular solvent. From the experimental evidence of the insensitivity of diffusion to mass as found in this and previous studies,^{14,15} it is reasonable to assume that the mass dependence of the correction factor and $\mu^{1/2}$ in eqn. (2) are largely nullified to yield

$$D_{12} \propto \frac{(D_{\text{SHS}}^0/D_{\text{E}}^0)}{(\sigma_1 + \sigma_2)^2 g_{12}} \quad (3)$$

where $(D_{\text{SHS}}^0/D_{\text{E}}^0)$ is a function of σ_1 only and can be given by a polynomial or quadratic equation in $1/\sigma_1$.

For mutual diffusion at infinite dilution, the unlike radial-distribution function at contact is given by the expression²⁴

$$g_{12} = \frac{1}{1-x} + \frac{3x\sigma_1}{(1-x)^2(\sigma_1 + \sigma_2)} + \frac{x^2\sigma_1}{2(1-x)^3\sigma_2} \quad (4)$$

where $x = \pi n_2 \sigma_2^3/6$. For a given solvent, eqn. (4) can be expressed by

$$g_{12} = \frac{k_1\sigma_1^2 + k_2\sigma_1 + k_3}{(\sigma_1 + \sigma_2)} \quad (5)$$

where k_1 , k_2 and k_3 are constants for a particular solvent. From eqn. (3) and (5), it follows that

$$D_{12} \propto \frac{1}{\sum_{i=0}^n C_i \sigma_1^i} \quad (6)$$

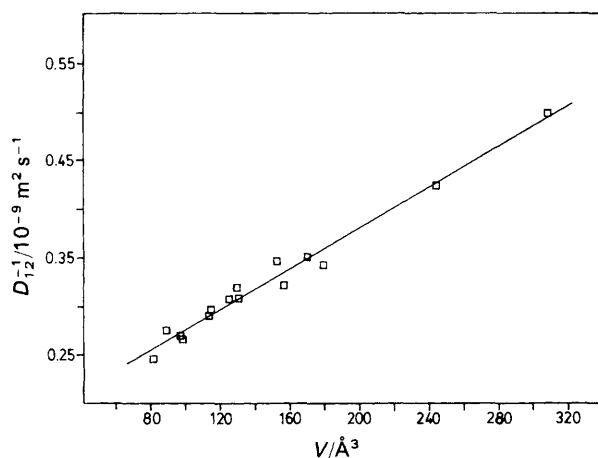


Fig. 1 Variation of D_{12}^{-1} with molecular volume of solutes diffusing in acetone at 298.2 K

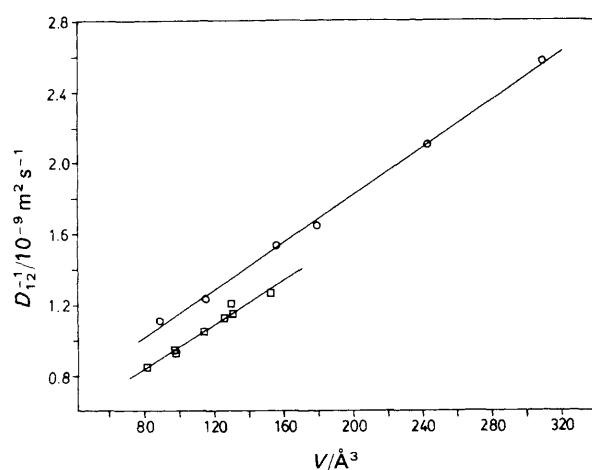


Fig. 2 Effect of solute shape on limiting mutual-diffusion in ethanol at 298.2 K. \circ , pseudo-spherical; \square , pseudo-planar

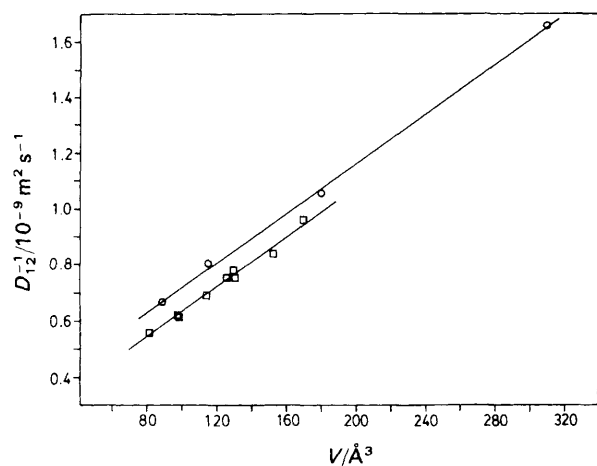


Fig. 3 Effect of solute shape on limiting mutual-diffusion in *n*-tetradecane at 298.2 K. \circ , pseudo-spherical; \square , pseudo-planar

where C_i is a constant. If V is the solute volume proportional to σ^3 , eqn. (6) can be represented alternatively by the following expression:

$$D_{12} \propto \frac{1}{V + C} \quad (7)$$

where C is the sum of all other order terms. Our experimental results in this work suggest that change in solute volume (in the range considered) leads to variation in C which is either small or insignificant as compared to V . This may be attributed in part to the fact that the use of a polynomial or quadratic equation to represent $D_{\text{SHS}}^{\sigma}/D_E^{\sigma}$ in eqn. (3) is unnecessary for a range of solute size that is not too wide.

For a short range of solute size, eqn. (7) may be written as

$$\frac{1}{D_{12}} = aV + b \quad (8)$$

where a and b are constants, and a plot of $1/D_{12}$ vs. V should yield a straight line. The linear relationship, however, is not expected for solutes with a wide range of molecular size.

Another major finding in this investigation is that the diffusion coefficients are dependent on the shape of solute molecules in ethanol and *n*-tetradecane, though the effect of solute shape on diffusion is insignificant in acetone. Fig. 2 and 3 indicate clearly that the pseudo-planar solutes diffuse faster than the pseudo-spherical solutes in ethanol and *n*-tetradecane. These results are consistent with those reported elsewhere.^{14,51,52} In this study, however, it appears that the effect of solute shape is greater as the size of solvent molecule becomes larger. One possible explanation is that when the solute size is small compared to the size of the solvent molecule, pseudo-planar solutes can slide between the solvent molecules easier than pseudo-spherical solutes. As an analogy, one can imagine that a flat matter can glide through a roller press much easier than a spherical object of the same size. When the solute size is large as compared to the solvent size, however, this slippery advantage for pseudo-planar molecules may be lost owing to solute rotations and steric effects. It is well known that non-spherical macromolecules actually diffuse slower than spherical macromolecules in common solvents.

According to eqn. (1), a comparison between the limiting mutual-diffusion coefficients for two solutes of the same size but different shape diffusing in a given solvent at constant temperature is actually a comparison between their translation-rotation coupling constants. Our data for ethanol and *n*-tetradecane thus indicate that A_{12} is greater for pseudo-planar than pseudo-spherical solutes.

It is of interest to compare the size of solvent molecules and the effects of solute shape on diffusion in this study. The VDW volumes of monomeric acetone, ethanol and *n*-tetradecane are 62.2, 51.0 and 236.9 Å³, respectively. Ethanol, however, is self-associated in the liquid state. The association number of ethanol is 2.82 as determined by the X-ray diffraction method at 293.2 K by Narten and Habenschuss.⁵³ It was found to decrease from 2.82 at 293.2 K to 1.85 at 554.0 K by Sun and Chen.⁴⁹ Based on these data, the association number for ethanol is estimated to be 2.80 at 298.2 K. In liquid, the molecular sizes are therefore *n*-tetradecane > associated ethanol > acetone, and the ratios are 3.8 : 2.3 : 1. It is therefore expected that the effect of solute shape on diffusion is greater in *n*-tetradecane than in ethanol and acetone. Our results show that pseudo-planar solutes on average diffuse faster than the pseudo-spherical solutes by ca. 17% in *n*-tetradecane and ca. 11% in ethanol. No significant effect of solute shape on diffusion is observed in acetone. A more complete understanding of the effects of shape on diffusion, however, awaits further experimental investigations.

Conclusion

We have demonstrated that experimental measurements of diffusion coefficients can provide straightforward and useful

information on the various molecular effects on diffusion. Our results have indicated that there exists a nearly linear relationship between the reciprocal of the diffusion coefficients and the molecular sizes of solutes studied. By comparing our data of pseudo-planar solutes with those of the pseudo-spherical molecules in the literature, it is found that the former diffuse *ca.* 17% faster than the latter in *n*-tetradecane and *ca.* 11% faster in ethanol, though no significant difference is noticed with acetone as solvent. The fact that the effects of solute shape on diffusion vary in different solvents provides a better understanding of the translation-rotation coupling constant in the RHS theory. It appears that the relative size of solvent and solute molecules is important in determining the value of the coupling constant.

Our data have also suggested that the mutual-diffusion coefficients are insensitive to the molecular mass and dipole moment of the solutes. We have shown that the linear relationship between the reciprocal of the diffusion coefficients and the molecular volume of the solutes in this study is comparable with the RHS theory. This correlation will be useful as a basis for elucidating the effects of molecular association on diffusion, which are currently under investigation in this laboratory.

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