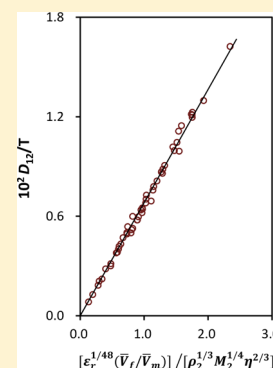


## Effect of Solvent on Diffusion: Probing with Nonpolar Solutes

T. C. Chan,\* Irene Lee, and K. S. Chan

Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

**ABSTRACT:** Limiting mutual diffusion coefficients of carbon tetrachloride in methanol and of benzene, toluene, naphthalene, and biphenyl in cyclohexane as well as in ethanol at different temperatures are reported. These new data, together with literature diffusivities for the same probe solutes and for solute mesitylene in various solvents, are utilized to elucidate the effect of solvent on diffusion. Here, the data are consistent with our recent findings [*J. Chem. Phys.* **2013**, *138*, 224503] on the effects of free volume fraction, molar density, molecular mass, and fractional viscosity of solvent on diffusion. The results in this study show that the relation developed previously for solvent dependence of diffusion of disc-shaped solutes is also valid for spherical carbon tetrachloride. It is further found in this investigation that diffusivities are weakly dependent on a solvent's dielectric constant. A relation that includes the dielectric effect of solvent is demonstrated to be capable of describing the solvent dependence of diffusion of the nonpolar solutes of different shapes and sizes in this work to within an average deviation of  $\pm 2.7\%$ . Comparisons with other diffusion models reveal that the newly developed relation is more accurate for representing the effect of solvent on diffusion. An expression for Zwanzig's "effective hydrodynamic radius" is also presented.



## 1. INTRODUCTION

Diffusion of molecules has long been extensively studied because of its importance in various areas of science and technology. As detailed motions of molecules in dense fluids are extremely complicated, diffusion in liquids remains up to now one of the most difficult and challenging problems in chemistry, physics, and other related disciplines. In particular, the effect of solvent on diffusion is still not well understood. Nonetheless, solvent plays a fundamental role in determining the diffusion rates of molecules in solutions, which are of immense significance to many diffusion-related studies as well as industrial processes and technologies.

There are different theories for accounting the diffusion behavior of molecules in dense fluids. Traditionally, diffusion in liquids is described by the hydrodynamic theory represented by the Stokes–Einstein–Sutherland relation, which is commonly known also as the Stokes–Einstein (SE) relation

$$D_{12} = \frac{k_B T}{C \pi r_1 \eta} \quad (1)$$

where  $D_{12}$  is the diffusion coefficient,  $k_B$  is the Boltzmann constant,  $T$  represents the absolute temperature,  $C$  is a number (4 for "slip" and 6 for "stick" boundary conditions),  $r_1$  refers to the radius of the diffusing molecule, and  $\eta$  is the viscosity of solvent. The SE relation was originally derived from the well-known Einstein relation

$$D_{12} = \frac{k_B T}{\xi} \quad (2)$$

where  $\xi$  refers to the frictional coefficient related to the retarding force acting on a diffusing particle by solvent in the diffusion process. Details of the SE relation has been reviewed by Tyrrell and Harris.<sup>1</sup> It should be pointed out that the

Einstein relation is generally recognized as a theoretically correct expression for diffusion, regardless of any mechanism for the friction.<sup>2</sup> By applying the Stokes law for the frictional coefficient  $\xi$  of a large spherical particle moving in a continuum of solvent medium, i.e.

$$\xi = C \pi r_1 \eta \quad (3)$$

the SE relation, eq 1, was thus established by combining eqs 2 and 3. For mutual diffusion at trace concentration (limiting mutual diffusion) of solutes, the SE relation can indeed describe diffusivities of large spherical solutes in solvent that contains smaller molecules quite well. Many experimental results<sup>3–10</sup> as well as computer simulations,<sup>11–14</sup> however, have found that the SE relation is invalid for solutes with sizes comparable to or smaller than the solvent molecules. Such sizes of solute and solvent molecules nonetheless exist commonly in real systems.

Recently there has been a great deal of interest in the use of fractional viscosity dependence for the studies of solvent dependence of diffusion in molecular and ionic liquids<sup>15–29</sup> as well as in diffusion-controlled reaction rates<sup>30</sup> and molecular relaxation processes.<sup>31</sup> This interest arose mainly as a result of the inapplicability of the SE relation for describing diffusion of solutes not large in size compared to solvent molecules. For a solute with a fixed radius, eq 1 can actually be rewritten for the solvent dependence of diffusion of the solute as

$$D_{12}/T = a_1 \eta^{-1} \quad (4)$$

where  $a_1$  is a solute-dependent constant. Except for large spherical solutes, numerous evidence<sup>4–10,15–32</sup> has shown that

Received: May 26, 2014

Revised: August 27, 2014

Published: August 27, 2014

diffusivity is dependent on a fractional power of the viscosity of solvent instead, i.e., for a given solute

$$D_{12}/T = a_2 \eta^{-t} \quad (5)$$

where  $a_2$  is a proportional constant and  $t$  is a number normally  $<1$  and generally around  $2/3$ .<sup>5,33</sup> The fact that eq 5 is more consistent with experimental data has been explained by the so-called “microviscosity” around a solute, i.e. the viscosity in the vicinity of a solute is different from the bulk viscosity of solvent.<sup>34</sup> Bagchi et al.<sup>33,35</sup> have further pointed out that decoupling of the solute motion from the structural relaxation of solvent could also lead to fractional viscosity dependence. Equation 5, a modification of the SE relation, is commonly referred to as the fractional Stokes–Einstein (FSE) relation in the literature.<sup>15,16</sup> It should be pointed out that quantitative theory of FSE is not yet available. In recent years, however, this relation has been extensively applied in different studies<sup>4–10,15–32</sup> of solvent dependence of diffusion and related processes. Although phenomenological description of collective dynamics of solvent molecules by use of FSE is simple and practical, nonetheless very few works have been done to critically evaluate the accurateness and applicability of the relation.

The kinetic theory is another important approach in the study of diffusion that has received considerable attention in recent years. In this theory, binary collisions of molecules are taken into account, and diffusivities in liquid phase are usually described in terms of molecular sizes and masses, temperature, number density, radial distribution function, free volume, translation-rotation coupling, and other molecular contributions. It should be noted that different kinetic models (e.g., Enskog and rough-hard-sphere models) have different expressions for describing diffusivities. Previous diffusion models of the kinetic theory have been reviewed also by Tyrrell and Harris.<sup>1</sup> In general, the kinetic theory of diffusion is more highly developed for dilute than for dense fluids, and it still appears that very few kinetic models of diffusion in liquids could be well validated by experimental diffusion data. In particular, it is generally recognized that the kinetic theory often overestimates the effect of molecular mass on diffusion.<sup>33,36</sup>

The primary difference between the two major diffusion theories above is that, while the hydrodynamic theory regards solvent as a continuum medium, the kinetic theory views it as a collection of discrete particles. Neither theories alone can satisfactorily describe diffusivities of solutes in a broad range of solvents and temperatures. To bridge the gap between theory and experimental facts, we have developed in a recent study<sup>37</sup> a relation capable of describing a total of 176 diffusion coefficients of nonassociated disc-like solutes for a broad range of solvents and temperatures to within an average absolute error of 2.8%. In that study, we have constructed a hydrodynamic-kinetic renormalized model, i.e., a relation that sees the solvent as having the dual properties of continuum and particles. Similar to the SE relation, the model has been built by a combination of two functions: one is dependent on solute and the other in terms of solvent properties. The function due to solvent encompassing temperature in that relation can be given by

$$D_{12} \propto \frac{(\bar{V}_f/\bar{V}_m)T}{\rho_2^{1/3} M_2^{1/4} \eta^y} \quad (6)$$

where  $\bar{V}_f/\bar{V}_m$  is the free volume fraction of the solvent,  $\rho_2$  represents the molar density (mass density/ $M_2$ ),  $M_2$  is the molar mass, and  $y$  is a fractional exponent similar to  $t$ . The free volume fraction is defined as

$$\bar{V}_f/\bar{V}_m = \frac{\bar{V}_m - N_A V_2}{\bar{V}_m} \quad (7)$$

where  $\bar{V}_m$  is the molar volume of a solvent,  $N_A$  is the Avogadro number, and  $V_2$  refers to the van der Waals volume of the solvent molecule. Equation 6 is basically an extension of the FSE relation by including molecular contributions. It has been formed by coupling FSE (developed from the hydrodynamic theory) with theoretical expressions<sup>38,39</sup> affiliated with the kinetic theory. The results of recent molecular dynamic simulations<sup>40</sup> have also been taken into account in the relation. It is noteworthy that each of the components in that relation has its own merits in other studies of smaller systems. Details of the development of the relation have already been discussed.<sup>37</sup> This molecular FSE (MFSE) relation has also been shown to be much more successful than the SE or FSE relations in the description of the solvent dependence of diffusion of disc-shaped solutes.<sup>37</sup> Nonetheless, it is not clear whether this relation is also applicable to solutes of other shapes or not.

In this work, we have measured tracer diffusivities (limiting mutual diffusion coefficients) of  $\text{CCl}_4$  in methanol as well as benzene, toluene, naphthalene, and biphenyl in ethanol and in cyclohexane at different temperatures. The nonpolar solutes chosen are different in shape and size, ranging from spherical ( $\text{CCl}_4$ ) to planar (benzene and naphthalene) and pseudoplanar (toluene and biphenyl). While the aromatic solutes are anisotropic solutes whose diffusion is affected by translation-rotation coupling,  $\text{CCl}_4$  is a spherical and totally symmetrical molecule whose diffusion is isotropic in any given solvent. It should be pointed out that many diffusion coefficients of the present probe solutes in different solvents are available in the literature for more objective and in-depth investigation. All aromatic solutes studied in this work are very thin disc-shaped molecules with aspect ratios approximately between 0.25 and 0.4 only. It has been shown by Bagchi et al.<sup>41</sup> that the effects of translation-rotation coupling on diffusion are about the same in a given solvent for disc-like molecules with values of aspect ratio between 0.25 and 0.5. The newly measured data, together with literature diffusivities for the probe solutes as well as for mesitylene in a wide range of solvents and temperatures, are used to unravel the effect of solvent on diffusion. There are three objectives in this study. First, it is of interest to find out if the relation developed in our previous work<sup>37</sup> for solvent dependence of diffusion of disc-shaped solutes is also valid for the spherical solute  $\text{CCl}_4$ . The second objective is to examine the dielectric effect of solvent, if any, on diffusion. It should be noted that evidence has been reported in the literature<sup>18,19</sup> that diffusivity can be correlated with dielectric relaxation time of solvent. Finally, it is hoped that an expression for Zwanzig's solvent-dependent “effective hydrodynamic radius”<sup>2</sup> can be obtained.

## 2. EXPERIMENTAL SECTION

Tracer diffusivities were measured by using the chromatographic peak-broadening technique, which is also known as the Taylor dispersion method. The experimental setup and instruments used were the same as reported in our previous study.<sup>37</sup> In this work, the solvents methanol (99.9%+, Aldrich),

Table 1. Experimental and Calculated  $D_{12}$  ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) for Spherical  $\text{CCl}_4$  in Different Solvents

solvent					solvent					
$[V_2 \text{ (} 10^{-24} \text{ cm}^3\text{)}, ^a M_2 \text{ (g mol}^{-1}\text{)}]$	$T \text{ (K)}$	exp $D_{12}^b$	refs	calc $D_{12}^c$	$[V_2 \text{ (} 10^{-24} \text{ cm}^3\text{)}, ^a M_2 \text{ (g mol}^{-1}\text{)}]$	$T \text{ (K)}$	exp $D_{12}^b$	refs	calc $D_{12}^c$	
methanol [34.82, 32.04]	278.15	$1.66 \pm 0.02$	this work	1.71	benzene [81.10, 78.11]	373.15	$6.06 \pm 0.06$	7	6.00	
	283.15	$1.76 \pm 0.02$	3	1.85		283.15	$1.47 \pm 0.02$	52	1.54	
	288.15	$1.96 \pm 0.02$	this work	2.00		298.15	1.94	4,52	1.96	
	298.15	$2.26 \pm 0.02^d$	this work	2.30		298.41	$1.92 \pm 0.02$	52	1.97	
	313.15	$2.84 \pm 0.03$	this work	2.81		313.15	$2.44 \pm 0.03$	52	2.44	
	323.15	$3.29 \pm 0.03$	this work	3.19		<i>n</i> -tetradecane [236.9, 198.4]	298.15	$0.897 \pm 0.006$	32	0.944
	333.15	$3.82 \pm 0.03$	8	3.60			313.15	$1.20 \pm 0.02$	32	1.21
	288.15	$1.092 \pm 0.004$	48	1.09			343.15	$1.81 \pm 0.02$	7	1.89
carbon tetrachloride [89.90, 153.8]	293.15	$1.18^e$	49	1.18		374.15	$2.59 \pm 0.05$	7	2.81	
	298.15	1.29	48,50	1.27		<i>n</i> -decane [172.2, 142.3]	298.15	$1.72 \pm 0.02$	46	1.79
	303.15	$1.428 \pm 0.006$	48	1.37			333.15	$2.89 \pm 0.02$	7	2.87
	313.15	$1.683 \pm 0.007$	48	1.57	373.15		$4.58 \pm 0.05$	7	4.47	
	323.15	$1.937 \pm 0.008$	48	1.79	acetone [62.24, 58.08]	283.15	$2.81 \pm 0.02$	3	2.99	
	283.15	$0.237 \pm 0.002$	3	0.238		298.15	$3.61 \pm 0.03$	46	3.57	
1-octanol [148.0, 130.2]	298.15	$0.381 \pm 0.002$	3	0.380	298.30	3.57	53	3.58		
	313.15	$0.576 \pm 0.006$	32	0.575	2-propanol [67.16, 60.10]	283.15	$0.629 \pm 0.008$	32	0.638	
	353.15	$1.48 \pm 0.01$	8	1.43	298.15	$0.936 \pm 0.018$	3	0.95		
	391.15	$2.75 \pm 0.02$	8	2.72	acetonitrile [45.82, 41.05]	298.15	3.32	3	3.13	
	cyclohexane [97.02, 84.16]	298.15	1.49	50,51	1.60	<i>n</i> -hexane [107.5, 86.18]	298.15	3.87	32,54,55	3.94
		308.15	$1.78 \pm 0.02$	50	1.86					
313.25		$2.00 \pm 0.04$	51	2.01	toluene [97.63, 92.14]	298.15	$2.17 \pm 0.02$	55	2.10	
333.35		$2.71 \pm 0.03$	51	2.72						
1-butanol [83.33, 74.12]	353.75	$3.70 \pm 0.04$	51	3.65						
	283.15	$0.591 \pm 0.002$	32	0.553						
	298.15	$0.843 \pm 0.004$	3	0.787						
	333.15	$1.67 \pm 0.02$	8	1.63						
<i>n</i> -octane [139.9, 114.2]	373.15	$3.30 \pm 0.01$	8	3.27						
	298.15	$2.56 \pm 0.02$	7	2.61						
	313.15	$3.12 \pm 0.02$	7	3.14						
	333.15	$4.05 \pm 0.04$	7	3.96						

<sup>a</sup>Calculated from group increments in Table 2 (see method in ref 45)

<sup>b</sup>Average value where two or more references are given. <sup>c</sup>Calculated from eq 12. <sup>d</sup>Compared with the values of 2.25, 2.27, and 2.248 in ref 3, 46, and 47, respectively. <sup>e</sup>Estimated from plot in ref 49.

<sup>a</sup>Calculated from group increments in Table 2 (see method in ref 45).<sup>b</sup>Average value where two or more references are given. <sup>c</sup>Calculated from eq 12. <sup>d</sup>Compared with the values of 2.25, 2.27, and 2.248 in refs 3, 46, and 47, respectively. <sup>e</sup>Estimated from plot in ref 49.

ethanol (99.8%+, E. Merck), and cyclohexane (99.9%+, Aldrich) were first degassed in an ultrasonic bath and then filtered with a 20  $\mu\text{m}$  stainless-steel solvent filter before use. The solutes carbon tetrachloride (99.9%, Aldrich), benzene (99.9%+, Aldrich), toluene (99.5%, E. Merck), naphthalene (99% BDH), and biphenyl (99%+, Koch-Light) were used as received. The solutes chosen are all nonpolar molecules incapable of forming strong association with common solvent molecules. They are, however, different in size and shape. The technique and procedures for the measurements were similar to those described previously.<sup>37,42</sup> Briefly, a capillary diffusion tube coiled in a circle with a diameter of about 23 cm was placed in a constant-temperature bath (Julabo model FP45). The diffusion tube was a 91.4 m long 304 stainless-steel tubing of 0.762 mm i.d. and 1.59 mm o.d. (Supelco). Temperatures of the bath were controlled to within  $\pm 0.01$  K and measured by a certified thermometer (Baird and Tatlock, no. GDZ27736). A dilute sample of 20–50  $\mu\text{L}$  was injected by an injection valve into a stream of solvent in the diffusion tube, the flow of which was delivered by an Agilent HPLC pump (model 1100) with a flow-rate precision of  $\pm 0.5\%$ . To ensure laminar flow, the solvent flow-rate was adjusted so that the constant volume flow was about 0.10 to 0.16 mL/min only. It has been shown by Taylor<sup>43</sup> that a combination of flow and diffusion can lead to a Gaussian distribution of solute along the capillary tube. At the end of the diffusion tube, the solute dispersion peak was detected by a

differential refractometer (Shimadzu model RID-10A). The tracer diffusivities were determined by the following relation:<sup>44</sup>

$$D_{12} = 0.2310R^2t_r/(W_{1/2})^2 \quad (8)$$

where  $R$  is the internal radius of the diffusion tube,  $t_r$  refers to the residence time of the solute in the tube, and  $W_{1/2}$  is the width at half-height of the eluted peak. In the present experiment, at least four measurements were made to obtain a diffusivity, and the average experimental error is generally about  $\pm 1\%$ .

### 3. RESULTS AND DISCUSSION

The measured limiting mutual diffusion coefficients of spherical carbon tetrachloride in methanol are given in Table 1. The uncertainty listed is the average absolute error of the measurements. Also displayed in this table are the diffusivities of  $\text{CCl}_4$  in other solvents at different temperatures, which were obtained from different sources in the literature. Since literature diffusivities of  $\text{CCl}_4$  in polar solvents of high dielectric constants are not as common as those in nonpolar solvents of low dielectric constants, diffusivities in polar methanol were thus measured in this work to provide more data in polar solvents for a balanced and objective study of the solvent dependence of diffusion. For reasons (in relation to standard state) given before,<sup>37</sup> only diffusivities measured below the normal boiling point of solvent under 1 atm were collected for the present study. There are a total of 51 diffusivities of  $\text{CCl}_4$  in 15 different

solvents in Table 1. The solvent molecules are of different sizes, shapes, and chemical natures. The solvent viscosities range from 0.249 to 13.03 mPa s, the temperatures vary from 278.15 to 391.15 K, and dielectric constants are from 1.84 to 36.26. Table 1 also lists the van der Waals volume ( $V_2$ ) and the molar mass ( $M_2$ ) for each of the solvents involved. The van der Waals (VDW) volumes were calculated from group increments, which are shown in Table 2.

**Table 2. Group Increments for van der Waals Volumes of Molecules**

group	volume ( $10^{-24}$ cm <sup>3</sup> ) <sup>a</sup>
–H (aliphatic)	5.25
–H (aromatic)	4.88
–Cl (aliphatic)	21.06
–Cl (aromatic)	20.96
–CH <sub>3</sub>	21.42
–CH <sub>2</sub> –	16.17
>C<	5.66
–OH	13.4 <sup>b</sup>
–CN	24.4 <sup>b</sup>
>C=O	19.4 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> –(phenyl)	76.22

<sup>a</sup>Average value from sources given in ref 45, except where noted otherwise. <sup>b</sup>From ref 56.

The measured diffusivities of planar benzene and naphthalene, along with those of pseudoplanar toluene and biphenyl, in ethanol and in cyclohexane at different temperatures are presented in Table 3. The measurements in ethanol and cyclohexane were made to provide more data in both polar and nonpolar solvents, which are useful for our study of the dielectric effect of solvent on diffusion. In addition to the data in Table 3, other literature diffusivities of the above disc-like solutes as well as mesitylene in different solvents have already been collected and displayed in ref 37. These diffusivities in a broad range of solvents and temperatures, which are not listed again in this work, are combined with our measured data for analysis and investigation of the effect of solvent on diffusion in liquids. The total numbers of diffusion data of benzene, toluene, naphthalene, and biphenyl for this study are 35, 30, 23, and 20, respectively. The different solvents involved are 16 for benzene, 14 for toluene, 9 in the case of naphthalene, and 11 for biphenyl. It should be noted that viscosity, density, and other physical properties (except molar mass and VDW volume) of

solvents are all different at different temperatures. Although we have not measured any new data for mesitylene, nonetheless the 14 literature diffusivities in seven different solvents at various temperatures are also utilized in this investigation. These data, which have been given in our earlier work,<sup>37</sup> were either directly measured in our laboratory or collected from the literature.

**3.1. Stokes–Einstein (SE) Relation.** The tracer diffusivities determined by Taylor's dispersion method in this work, together with those obtained from various studies in the literature, were used to test the SE relation. Viscosity values of various solvents at different temperatures are displayed in Table 4. By using the dimensionless data as shown in Tables 1, 3, and 4 as well as those in ref 37, we have found that eq 4 is only able to describe each of the six sets of solute diffusion data to an average error around  $\pm 12.7\%$ , ranging from  $\pm 10.3\%$  for mesitylene to about  $\pm 14.9\%$  in the case of carbon tetrachloride. The maximum absolute deviations for benzene, toluene, naphthalene, mesitylene, biphenyl, and carbon tetrachloride are 48.3, 41.1, 42.0, 44.1, 40.8, and 62.3%, respectively. These results are clearly unsatisfactory, and they further verify the inapplicability of the SE relation for solutes that are not large compared to solvent molecules. It should be noted that Zwanzig and Harrison<sup>2</sup> have previously proposed a solvent-dependent "effective hydrodynamic radius" (EHR) for saving the SE relation. Nonetheless, detailed expression for it is not yet available in the literature. Unless SE can be modified (e.g., with EHR), the relation as it is given by eq 4 is evidently unsuitable for representing the solvent dependence of diffusion in this study. More discussion on the expression for EHR is provided in section 3.5.

**3.2. Analysis of Fractional Stokes–Einstein (FSE) Relation.** There has been a great deal of evidence<sup>4–10,15–32</sup> that eq 5 of the FSE relation is more suitable than the SE relation for describing the solvent dependence of diffusion and related molecular processes. The logarithm form of this equation can be expressed as

$$\ln(D_{12}/T) = \ln a_2 - t \ln \eta \quad (9)$$

We have applied eq 9 for correlating the data (without units) of the six probe solutes in this investigation. A linear regression finds that the data of spherical solute CCl<sub>4</sub> in Table 1 can be predicted to an average error of  $\pm 8.6\%$ , with the maximum absolute deviation at 29.6%. For each of the disc-like solutes studied, diffusivities can be similarly described by FSE to an average error within  $\pm 7.3\%$ , whereas the maximum absolute

**Table 3. Experimental  $D_{12}$  ( $10^{-9}$  m<sup>2</sup> s<sup>-1</sup>) of Disc-Shaped Solute in Cyclohexane and Ethanol at Different Temperatures**

solvent	T (K)	benzene	toluene	naphthalene	biphenyl
cyclohexane	288.15	1.53 $\pm$ 0.02	1.41 $\pm$ 0.02	1.18 $\pm$ 0.01	1.07 $\pm$ 0.01
	298.15	1.89 <sup>a</sup>	1.72 $\pm$ 0.02 <sup>b</sup>	1.44 $\pm$ 0.01 <sup>a</sup>	1.28 $\pm$ 0.02 <sup>a</sup>
	308.15	2.20 $\pm$ 0.02	2.03 $\pm$ 0.02	1.71 $\pm$ 0.01	1.52 $\pm$ 0.02
	318.15	2.55 $\pm$ 0.03	2.36 $\pm$ 0.03	2.01 $\pm$ 0.02	1.78 $\pm$ 0.02
	328.15	2.94 $\pm$ 0.03	2.73 $\pm$ 0.03	2.33 $\pm$ 0.02	2.07 $\pm$ 0.02
	333.15	3.18 $\pm$ 0.02 <sup>c</sup>	2.968 $\pm$ 0.006 <sup>c</sup>	2.51 $\pm$ 0.02 <sup>c</sup>	
ethanol	268.15	0.985 $\pm$ 0.009	0.904 $\pm$ 0.008	0.734 $\pm$ 0.008	0.648 $\pm$ 0.007
	283.15	1.35 $\pm$ 0.01	1.23 $\pm$ 0.01	1.01 $\pm$ 0.01	0.910 $\pm$ 0.009
	298.15	1.79 $\pm$ 0.01 <sup>d</sup>	1.62 $\pm$ 0.02 <sup>d</sup>	1.33 $\pm$ 0.01 <sup>e</sup>	1.20 $\pm$ 0.01 <sup>f</sup>
	313.15	2.31 $\pm$ 0.02	2.10 $\pm$ 0.02	1.76 $\pm$ 0.02	1.58 $\pm$ 0.02
	328.15	2.96 $\pm$ 0.03	2.70 $\pm$ 0.03	2.29 $\pm$ 0.02	2.03 $\pm$ 0.02

<sup>a</sup>From ref 37. <sup>b</sup>Average value from refs 37 and 57. <sup>c</sup>From ref 57. <sup>d</sup>From ref 58. <sup>e</sup>Compared with 1.32 in ref 58. <sup>f</sup>From ref 59.



Table 4. Values of  $\eta$ ,  $d$ ,  $\epsilon_r$ ,  $\rho_2$ , and  $\bar{V}_f/\bar{V}_m$  of Solvents at Different Temperatures

temp (K)	solvent	$\eta$ (m Pa s) <sup>a</sup>	$d$ (g cm <sup>-3</sup> ) <sup>a</sup>	$\epsilon_r$ <sup>b</sup>	$\rho_2$ (10 <sup>-3</sup> mol cm <sup>-3</sup> )	$\bar{V}_f/\bar{V}_m$
268.15	ethanol	1.970	0.8142	28.91	17.67	0.4573
273.15	<i>n</i> -hexane	0.379	0.6784	1.913	7.872	0.4904
278.15	methanol	0.721	0.8050	36.26	25.12	0.4732
280.15	<i>n</i> -heptane	0.477	0.6966	1.939	6.952	0.4821
283.15	acetone	0.355	0.8028	22.24	13.82	0.4819
	benzene	0.773	0.8876	2.297	11.36	0.4450
	1-butanol	3.841 <sup>b</sup>	0.8183	19.39	11.04	0.4460
	ethanol	1.418	0.8010	26.74	17.39	0.4661
	methanol	0.667	0.8006	35.25	24.99	0.4760
	1-octanol	13.03 <sup>b</sup>	0.8340	11.06	6.406	0.4291
	2-propanol	3.269 <sup>b</sup>	0.7970	21.75	13.26	0.4637
288.15	carbon tetrachloride	1.034	1.602	2.248	10.42	0.4361
	cyclohexane	1.051	0.7820	2.032	9.292	0.4571
	methanol	0.619	0.7962	34.31	24.85	0.4789
293.15	carbon tetrachloride	0.960	1.593	2.238	10.36	0.4392
298.15	acetone	0.308	0.7856	20.49	13.53	0.4930
	acetonitrile	0.347	0.7793	35.69	18.98	0.4762
	benzene	0.606	0.8729	2.271	11.18	0.4542
	1-butanol	2.544 <sup>b</sup>	0.8062	17.33	10.88	0.4542
	carbon tetrachloride	0.893	1.583	2.228	10.29	0.4428
	chlorobenzene	0.742 <sup>c</sup>	1.101	5.697	9.778	0.4276
	cyclohexane	0.901	0.7731	2.016	9.186	0.4633
	<i>n</i> -decane	0.851 <sup>c</sup>	0.7284	1.985	5.119	0.4692
	<i>n</i> -dodecane	1.390	0.7450	2.006	4.375	0.4613
	ethanol	1.057	0.7873	24.85	17.09	0.4752
	<i>n</i> -heptane	0.390	0.6816	1.911	6.802	0.4933
	<i>n</i> -hexadecane	3.063	0.7701	2.040	3.402	0.4486
	<i>n</i> -hexane	0.296	0.6563	1.882	7.615	0.5070
	methanol	0.539	0.7872	32.61	24.57	0.4848
	<i>n</i> -octane	0.511	0.6986	1.941	6.117	0.4846
	1-octanol	7.288 <sup>b</sup>	0.8230	9.863	6.321	0.4366
	2-propanol	2.038 <sup>b</sup>	0.7827	19.26	13.02	0.4733
	<i>n</i> -tetradecane	2.128 <sup>b</sup>	0.7578	2.028	3.820	0.4551
	toluene	0.554 <sup>c</sup>	0.8647	2.374	9.385	0.4482
298.30	acetone	0.308	0.7854	20.48	13.52	0.4931
298.41	benzene	0.603	0.8727	2.270	11.17	0.4543
299.15	<i>n</i> -hexane	0.293	0.6554	1.881	7.605	0.5077
303.15	carbon tetrachloride	0.834	1.574	2.218	10.23	0.4459
	<i>n</i> -heptane	0.371	0.6773	1.904	6.760	0.4965
	<i>n</i> -octane	0.482	0.6947	1.934	6.083	0.4875
308.15	benzene	0.524	0.8629	2.253	11.05	0.4605
	cyclohexane	0.774	0.7641	2.001	9.079	0.4695
313.15	benzene	0.490	0.8579	2.244	10.98	0.4636
	carbon tetrachloride	0.733	1.556	2.198	10.12	0.4523
	ethanol	0.810	0.7731	23.22	16.78	0.4847
	<i>n</i> -heptane	0.336	0.6687	1.889	6.674	0.5029
	<i>n</i> -hexane	0.259	0.6425	1.861	7.455	0.5174
	methanol	0.447	0.7733	30.55	24.14	0.4939
	<i>n</i> -octane	0.432	0.6868	1.921	6.014	0.4933
	1-octanol	4.382 <sup>b</sup>	0.8119	8.762	6.236	0.4442
	<i>n</i> -tetradecane	1.623 <sup>b</sup>	0.7485	2.011	3.773	0.4618
313.25	cyclohexane	0.717	0.7594	1.993	9.023	0.4728
318.15	cyclohexane	0.666	0.7549	1.985	8.970	0.4759
323.15	carbon tetrachloride	0.650	1.537	2.178	9.993	0.4590
	<i>n</i> -heptane	0.306	0.6600	1.874	6.587	0.5093
	methanol	0.398	0.7638	29.50	23.84	0.5001
328.15	cyclohexane	0.574	0.7455	1.969	8.858	0.4824
	ethanol	0.634	0.7584	21.82	16.46	0.4945
333.15	1-butanol	1.106	0.7764	13.23	10.47	0.4743
	cyclohexane	0.534	0.7408	1.961	8.802	0.4857
	<i>n</i> -decane	0.542 <sup>c</sup>	0.7019	1.940	4.933	0.4885

Table 4. continued

temp (K)	solvent	$\eta$ (m Pa s) <sup>a</sup>	$d$ (g cm <sup>-3</sup> ) <sup>a</sup>	$\epsilon_r$ <sup>b</sup>	$\rho_2$ (10 <sup>-3</sup> mol cm <sup>-3</sup> )	$\bar{V}_f/\bar{V}_m$
333.35	<i>n</i> -heptane	0.281	0.6510	1.860	6.497	0.5160
	<i>n</i> -hexane	0.219	0.6234	1.831	7.234	0.5317
	methanol	0.357	0.7539	28.71	23.53	0.5066
	<i>n</i> -octane	0.353	0.6706	1.894	5.872	0.5053
	2-propanol	0.806 <sup>b</sup>	0.7472	14.20	12.43	0.4972
343.15	cyclohexane	0.532	0.7406	1.961	8.800	0.4858
	<i>n</i> -heptane	0.258	0.6419	1.846	6.406	0.5228
353.15	<i>n</i> -tetradecane	1.021 <sup>b</sup>	0.7295	1.975	3.677	0.4754
	<i>n</i> -heptane	0.237	0.6325	1.832	6.312	0.5298
353.75	1-octanol	1.478 <sup>c</sup>	0.7811	6.296	5.999	0.4653
	cyclohexane	0.397	0.7207	1.928	8.563	0.4997
373.15	1-butanol	0.514	0.7396	9.621	9.978	0.4993
	<i>n</i> -decane	0.365 <sup>c</sup>	0.6699	1.891	4.708	0.5118
374.15	<i>n</i> -octane	0.249	0.6362	1.839	5.571	0.5307
	<i>n</i> -tetradecane	0.689 <sup>b</sup>	0.7091	1.938	3.574	0.4901
391.15	1-octanol	0.723 <sup>b</sup>	0.7502	4.585	5.762	0.4865

<sup>a</sup>Calculated values from ref 60, excepted where noted otherwise. <sup>b</sup>Calculated from ref 61. <sup>c</sup>Average values from refs 60 and 61.

Table 5. Results of Linear Regression of FSE using eq 9 for Solute in Each Solvent at Different Temperatures

solute	solvent	no. of data	range of temp (K)	$a_2$ (10 <sup>-3</sup> )	$t$	correl. coef.	av. devi. (±%)	max. abs. devi. (%)
CCl <sub>4</sub>	methanol	7	278.2–333.2	4.32 ± 0.07	0.934 ± 0.022	0.9971	1.14	1.84
	carbon tetrachloride	6	288.2–323.2	3.89 ± 0.02	1.013 ± 0.023	0.9979	0.72	0.90
	cyclohexane	5	298.2–353.8	4.62 ± 0.07	0.892 ± 0.028	0.9971	1.12	2.59
	1-octanol	5	283.2–391.2	5.54 ± 0.04	0.739 ± 0.004	0.9999	0.58	1.20
benzene	cyclohexane	6	288.2–333.2	5.68 ± 0.07	0.838 ± 0.033	0.9938	1.36	2.60
	<i>n</i> -heptane	6	298.2–353.2	5.64 ± 0.27	0.870 ± 0.039	0.9919	1.15	2.05
	ethanol	5	268.2–328.2	6.27 ± 0.01	0.790 ± 0.004	0.9999	0.19	0.45
	<i>n</i> -hexane	5	273.2–333.2	5.07 ± 0.21	0.925 ± 0.032	0.9964	0.91	1.38

deviations are from 21.7% (mesitylene) to 33.4% (benzene). These results of FSE are indeed much improved over those of the SE relation, which have already been given and discussed in section 3.1. In consideration of the precision (generally about ±1%) of the experimental diffusivities collected, however, the results of the FSE relation for the probe solutes still cannot be regarded as good. It should be pointed out that there are four sets of solvent system, each with five or more diffusion data at different temperatures for carbon tetrachloride (see in Table 1) as well as for benzene (see in Table 3 and ref 37). It is interesting to correlate  $D_{12}/T$  with  $\eta$  by using FSE for data of solute in a single solvent. Table 5 displays the statistics and results of linear regression for each set of such data of solutes CCl<sub>4</sub> and benzene. The FSE relation fits data for a solute in a single solvent generally well. As shown in the table, the average deviations are about ±1%, and the maximum absolute deviations are all within 2.6%. It is noteworthy that if FSE is general and valid, then the  $a_2$  and  $t$  values are supposed to be separate constants for diffusion of a given solute, irrespective of solvent. However, Table 5 shows that the  $a_2$  values are from 3.9 to 5.5 for CCl<sub>4</sub> and between 5.1 and 6.3 for benzene in different individual solvents. The  $t$  values also vary from 0.739 to 1.01 for CCl<sub>4</sub> and in the case of benzene from 0.790 to 0.925. In view of these fairly inconsistent results, it is unsurprising that the FSE relation could be satisfactory but not very accurate for representing the solvent dependence of diffusion of any solute in a broad range of solvents in this study, although it works very well for a given solvent. Nonetheless, FSE has its own merits, particularly that it is simple and useful for relating the viscosity dependence of diffusion. As shown in section 3.4, the

development of our improved relation (eq 12) in this work is actually based on the FSE relation.

As pointed out previously by Harris,<sup>16</sup> there are actually different forms of the FSE relation. One equation widely used in the literature, in addition to eq 5, is the following expression:

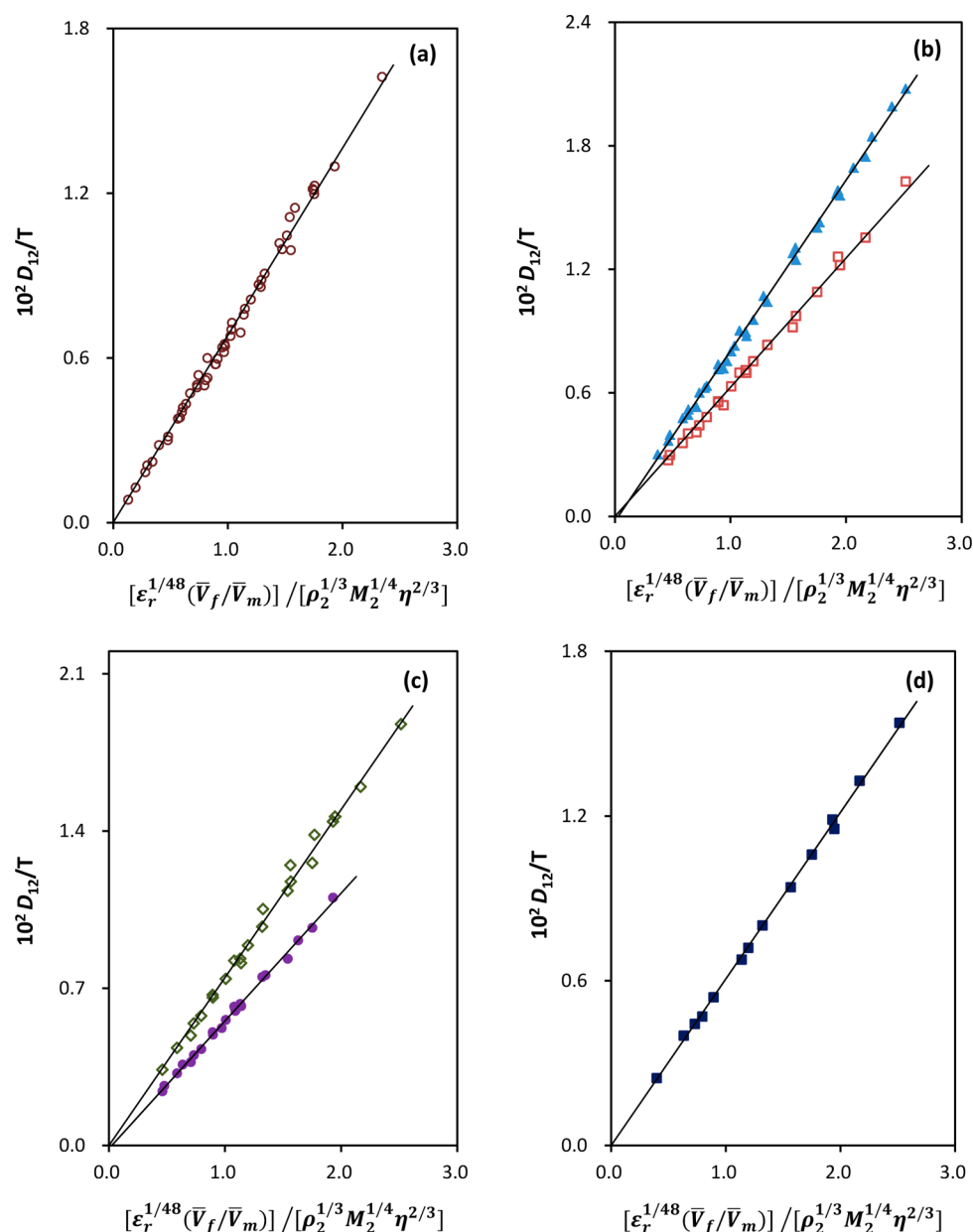
$$D_{12} = a_{22}(T/\eta)^s \quad (10)$$

where  $a_{22}$  is a solute-dependent constant, and  $s$  is a fractional exponent. We have also carried out fittings of the logarithm form of eq 10 to the 6 sets of solute data. The results, along with those of eq 5 of FSE as well as eq 2 of SE, are summarized in Table 6. From this table, it can be seen that the results of eq 5 is generally more satisfactory than those of eq 10, although the differences are small. In summary, although FSE (either eq 5 or eq 10) shows significant improvement over the SE relation (eq 2) for representing the solvent dependence of diffusion, it is nevertheless still inadequate in view of the overall precision of the data studied. Diffusion in liquids is generally known as a complex process that involves complicated molecular dynamics. Solvent dependence of diffusion probably cannot be sufficiently described by a single variable  $\eta$  only. Effects of other solvent properties may also be significant.

**3.3. Molecular FSE Relation.** In an attempt to mend the deficiency of the FSE relation, we have in a recent study<sup>37</sup> extended the FSE relation to include the molecular effects of solvents. This molecular FSE (MFSE) relation has been developed by combining FSE with theoretical expressions associated with the kinetic theory. The approach was based primarily on the fact that diffusion of nonmacromolecular solutes in liquids cannot be fully described by either the hydrodynamic theory or the kinetic model alone, i.e., solvent

Table 6. Comparisons of Different Relations for Solvent Dependence of Diffusion

	solute	SE		FSE		MFSE		this work	
		eq 4	eq 5	eq 10	eq 11	eq 12	eq 13		
proportional constant ( $10^{-3}$ )	carbon tetrachloride	$a_1 = 4.12 \pm 0.06$	$a_2 = 5.03 \pm 0.08$	$a_{22} = 23.1 \pm 2.7$	$a_3 = 6.98 \pm 0.05$	$a_4 = 6.73 \pm 0.04$	$a_5 = 6.82 \pm 0.03$		
	benzene	$4.77 \pm 0.07$	$6.04 \pm 0.13$	$22.1 \pm 3.4$	$8.31 \pm 0.06$	$8.03 \pm 0.05$	$8.13 \pm 0.03$		
	toluene	$4.42 \pm 0.09$	$5.51 \pm 0.12$	$20.3 \pm 3.5$	$7.65 \pm 0.06$	$7.38 \pm 0.05$	$7.47 \pm 0.04$		
	naphthalene	$3.68 \pm 0.08$	$4.59 \pm 0.09$	$15.8 \pm 2.6$	$6.39 \pm 0.06$	$6.13 \pm 0.05$	$6.28 \pm 0.04$		
	mesitylene	$3.49 \pm 0.07$	$4.46 \pm 0.13$	$16.2 \pm 3.3$	$6.38 \pm 0.07$	$6.08 \pm 0.04$	$6.07 \pm 0.02$		
exponent of viscosity	biphenyl	$3.35 \pm 0.09$	$4.07 \pm 0.09$	$16.8 \pm 3.5$	$5.70 \pm 0.05$	$5.50 \pm 0.03$	$5.56 \pm 0.03$		
	carbon tetrachloride	1	$0.717 \pm 0.018$	$0.734 \pm 0.019$	$0.678 \pm 0.008$	$0.681 \pm 0.006$	$2/3$		
	benzene	1	$0.757 \pm 0.024$	$0.772 \pm 0.024$	$0.666 \pm 0.009$	$0.674 \pm 0.007$	$2/3$		
	toluene	1	$0.761 \pm 0.028$	$0.771 \pm 0.028$	$0.672 \pm 0.011$	$0.680 \pm 0.010$	$2/3$		
	naphthalene	1	$0.771 \pm 0.026$	$0.783 \pm 0.026$	$0.680 \pm 0.012$	$0.689 \pm 0.010$	$2/3$		
av. deviation ( $\pm\%$ )	mesitylene	1	$0.768 \pm 0.031$	$0.774 \pm 0.032$	$0.646 \pm 0.012$	$0.662 \pm 0.007$	$2/3$		
	biphenyl	1	$0.738 \pm 0.034$	$0.751 \pm 0.035$	$0.678 \pm 0.014$	$0.682 \pm 0.010$	$2/3$		
	carbon tetrachloride	14.88	8.57	9.71	3.62	2.73	3.23		
	benzene	11.94	7.31	7.58	2.70	2.13	2.23		
	toluene	13.17	6.85	6.95	2.98	2.20	2.41		
max. abs. deviation (%)	naphthalene	12.72	5.07	5.59	2.64	2.18	2.41		
	mesitylene	10.26	5.20	5.66	2.15	1.33	1.31		
	biphenyl	13.27	6.32	6.86	2.53	1.87	1.97		
	carbon tetrachloride	62.27	29.62	31.81	10.84	8.49	9.43		
	benzene	48.30	33.38	33.43	8.66	6.54	7.92		
	toluene	41.05	27.44	27.47	8.52	6.47	7.63		
	naphthalene	41.97	24.32	24.39	8.31	7.27	9.30		
	mesitylene	44.11	21.67	21.83	6.08	3.69	3.87		
	biphenyl	40.76	22.94	22.88	6.60	4.16	5.84		



**Figure 1.** Solvent dependence of  $D_{12}/T$  for (a)  $\text{CCl}_4$ , (b) benzene  $\blacktriangle$  and naphthalene  $\square$ , (c) toluene  $\diamond$  and biphenyl  $\bullet$ , and (d) mesitylene; values shown are dimensionless based on data (without units) listed in Tables 1, 3, and 4 and in ref 37.

can neither be treated as hydrodynamic continuum nor discrete particles only. While each of the FSE and kinetic relations has their own merits, the combination of them provides complementary and synergistic effects for more realistic description. The solvent dependence developed in that MFSE relation is given by eq 6. For diffusion of a given solute in different solvents, eq 6 can be written as

$$D_{12}/T = \frac{a_3(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3} M_2^{1/4} \eta^y} \quad (11)$$

where  $a_3$  is a solute-dependent constant. It should be pointed out that the product  $\rho_2^{1/3} M_2^{1/4}$  in eq 11 is based on the theoretical result of March<sup>39</sup> with the effect of solvent's molecular mass being slightly reduced as it is generally recognized that the effect of mass on diffusion is fairly weak.<sup>33,36</sup> The weak dependence of diffusion on the mass of solvent molecule has also been demonstrated in a recent

molecular dynamic simulation study by Whitman et al.<sup>40</sup> The dependence on  $\bar{V}_f/\bar{V}_m$  in eq 11 is modified from Hildebrand's free volume theory of diffusion.<sup>38</sup> The concept of free volume theory is physically reasonable as availability of more free space would allow ease of diffusion and hence greater diffusivities of molecules. Details of the development of the MFSE relation have been given in ref 37.

We have tested eq 11 by using it to correlate the 6 sets of solute data in this study. Solvent properties such as density  $d$ , dielectric constant  $\epsilon_r$ , molar density  $\rho_2$ , and free volume fraction  $\bar{V}_f/\bar{V}_m$  are given in Table 4. The results of the values of  $a_3$ ,  $y$ , average error, and maximum absolute deviation are shown in Table 6. It can be seen from the results of the average errors and maximum deviations in this table that MFSE is a remarkable improvement over the SE and the FSE relations for describing the effect of solvent on diffusion. The present



work also demonstrates that eq 11 of MFSE is valid for solute molecules of different shapes in this study as well.

**3.4. Dielectric Effect.** Previously Quitevis and co-workers<sup>18,19</sup> showed in a holographic fluorescence recovery study that translational diffusivities can be correlated with dielectric relaxation time of solvent. A closer inspection of the diffusivities calculated by MFSE in this work indeed reveals that the values in polar solvents are slightly underestimated, while those in nonpolar solvents are generally overestimated. We have therefore carried out work to explore if MFSE could be improved by incorporating the dielectric effect of solvent. After several different attempts, a modified MFSE (MMFSE) relation has been obtained as follows:

$$D_{12}/T = \frac{a_4(\epsilon_r^{1/48})(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3}M_2^{1/4}\eta^z} \quad (12)$$

where  $a_4$  is a constant,  $\epsilon_r$  represents the dielectric constant (relative permittivity) of the solvent, and  $z$  is a fractional power of viscosity. The exponent of the relative permittivity in eq 12 is obtained by averaging the best fit values of the six solutes studied. The average value together with uncertainty is about  $1/(48 \pm 5)$ . It should be noted that the uncertainty in the exponent may cause a small average error of  $\pm 0.2\%$  in the calculated diffusion coefficients, which nonetheless is relatively insignificant as compared to the overall precision of the measured diffusion data in this study. The results of correlation rendered by eq 12 are given in Table 6 for all data studied. These results clearly indicate that there is indeed a dielectric effect of solvent on diffusion, as eq 12 shows consistent improvement over MFSE for describing the solvent dependence of diffusion for all (without exception) of the 6 sets of solute diffusivities studied in this work. Although the overall dielectric effect is relatively small as compared to other solvent effects in this work, the individual effect is nevertheless still significant. For example, there is a difference of about 6.4% in the calculated effect between  $\epsilon_r = 1.83$  and  $\epsilon_r = 36.3$ , i.e., the range of dielectric constants in this study. It should be noted that all solutes studied here are nonpolar. Dielectric effect of solvent on diffusion is probably due to “microdielectric constant” of solvent around a solute or to decoupling of the motion of solute from the dielectric relaxation of solvent. The effect should be more important for polar solutes. Diffusion of polar solutes, in particular those capable of hydrogen bonding, is a subject worthy of further experimental and theoretical investigations.

Comparisons between different diffusion models in Table 6 reveal that eq 12 is clearly the most accurate relation for describing the effect of solvent on diffusion. It should be pointed out that the data used in this study cover a wide range of tracer diffusivities in various solvents at different temperatures. The average errors of the diffusivities predicted by eq 12 for the six solutes are between  $\pm 1.33$  and  $\pm 2.73\%$ , which are fairly close to the overall precisions (about  $\pm 1\%$ ) of the experimental data studied. It is also noteworthy that the fractional exponent  $z$  values of the probe solutes in this study are found all nearly the same at around  $2/3$ . Similar result has been obtained for disc-like aromatic solutes of all sizes in our recent study.<sup>37</sup> Whether this result holds well for other spherical solutes of different sizes or not, however, is a subject under current investigation in our laboratory. Although our preliminary result indicates that value of  $z$  increases with size of spherical solutes, it is nevertheless of interest to observe that it

is also around  $2/3$  for  $\text{CCl}_4$  in this study, in particular of the fact that while the disc-shaped aromatic solutes with small aspect ratios are anisotropic compounds,  $\text{CCl}_4$  is a spherical and totally symmetrical solute. By replacing  $z$  with  $2/3$  in eq 12, i.e., by using the relation

$$D_{12}/T = \frac{a_5(\epsilon_r^{1/48})(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3}M_2^{1/4}\eta^{2/3}} \quad (13)$$

where  $a_5$  is a solute-dependent constant, we have found it almost equally well for describing the diffusion data, especially those of the disc-shaped solutes in this work. The results are presented also in Table 6. A worthy remark is that there is only one parameter  $a_5$  in eq 13. The present results of eq 13 for all solutes studied are plotted in Figure 1.

**3.5. Molecular Stokes–Einstein Relation and Effective Hydrodynamic Radius.** The success of eq 12 and likewise eq 13 is due primarily to the addition of the molecular effects of solvent to the FSE relation. It demonstrates that the particle nature of a solvent becomes significant when diffusion of nonmacromolecular solutes cannot be described by a hydrodynamic theory, namely the SE relation. Previously, Zwanzig and Harrison<sup>2</sup> argued that the fractional viscosity dependence of FSE is not theoretically correct as compared to the SE relation. The authors further suggested to preserve the standard form of the SE relation by using a solvent-dependent “effective hydrodynamic radius” (EHR) instead of  $r_1$  in eq 1, i.e., by the following relation:

$$D_{12} = \frac{k_B T}{C\pi R_e \eta} \quad (14)$$

where  $R_e$  is the EHR. Unfortunately, quantitative expression for EHR is not yet given in the literature. It is of interest to point out that eq 13 can be alternatively written as

$$D_{12}/T = \frac{a_5(\epsilon_r^{1/48})(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3}M_2^{1/4}(\eta^{-1/3})\eta} \quad (15)$$

By combining eq 14 and eq 15, it can be shown that

$$R_e = \frac{a_6 \rho_2^{1/3} M_2^{1/4} (\eta^{-1/3})}{(\epsilon_r^{1/48})(\bar{V}_f/\bar{V}_m)} \quad (16)$$

where  $a_6$  is equal to  $k_B/(a_5 C \pi)$ . Equation 16 is a general expression for EHR of the 6 probe solutes in this study. When eq 16 is substituted back into eq 14, the result is a “molecular Stokes–Einstein” relation equivalent to eq 13 as well as eq 15, which satisfies the EHR version of the SE relation suggested by Zwanzig and Harrison.<sup>2</sup> From the consistently accurate results of this study, it can be seen that the expression for EHR of a particular solute is generally applicable to all solvents in the present work, although the parameter  $a_6$  is solute-dependent. The value of  $a_6$  as well as  $a_5$  should be dependent on the size and shape of the solute particle. For a given solute, however, the value of EHR is different in different solvents, even when the temperature is the same.

## 4. CONCLUSION

Experimental diffusivities are immensely important for understanding the diffusion behavior of molecules in liquids. Diffusion theories can often be compared and thus improved through prediction of and agreement with experimental facts. Currently there appears a lack of general theories that can

satisfactorily describe diffusion data of solutes which are not very large as compared to solvent molecules. In particular, the effect of solvent on diffusion of such solutes is still not clear. Here, we report new diffusion coefficients of spherical carbon tetrachloride in methanol as well as disc-shaped benzene, toluene, naphthalene, and biphenyl in cyclohexane and in ethanol at different temperatures. The precisely measured data are combined with literature diffusivities of the same solutes and of mesitylene in various solvents to probe the effect of solvent on diffusion.

Attempts have been made in this study to correlate and analyze the experimental data of each of the nonpolar solutes with different diffusion models in the literature. It is found that the SE relation is inapplicable and the FSE relation inadequate for representing the solvent dependence of diffusion. These relations interpret the effect of solvent on diffusion only in terms of either viscosity or fractional power of viscosity. A molecular FSE relation developed in our previous study,<sup>37</sup> which includes the effects of molar mass, molar density, and free volume fraction of solvent, shows significant improvement over the SE and the FSE relations for describing the solvent dependence of diffusion of solutes with different sizes and shapes in this work. We also contribute here our finding of a weak but nevertheless significant effect of solvent's dielectric constant on diffusion. A most accurate relation for describing the effect of solvent on diffusion is given by eq 12. All six sets of solute diffusion data in this investigation are remarkably well described (within an average error of  $\pm 2.73\%$ ) by this new relation which combines FSE with the molecular effects, including dielectric effect, of solvent. A total of 173 data of the six solutes has been studied. The data cover various solvents with viscosities ranging from 0.219 to 13.03 mPa s and different temperatures from 268.2 to 391.2 K. Solvent molecules are also different in shape, size, and chemical nature. Because of the more accurate prediction of the solvent dependence of diffusion, eq 12 should be useful for future studies of diffusion in liquids as well as rates of chemical reactions and molecular relaxation processes.

Equation 13, a simplification of eq 12 with a fixed value of 2/3 as the fractional power of viscosity, is also shown in this work to be nearly as good as eq 12 for representing the solvent dependence of diffusion of all solutes studied, in particular the disc-shaped solutes. By using this simple relation with only one solute-dependent parameter, we have further constructed a molecular Stokes–Einstein relation (eq 15) that can yield an expression for Zwanzig's "effective hydrodynamic radius".<sup>2</sup> The success of eq 15 or its equivalent verifies that an approach that incorporates particle nature of solvent in a hydrodynamic model is significant for describing and understanding the real effect of solvent on diffusion of solutes with sizes small or comparable to solvent molecules, while such effect cannot be satisfactorily realized in terms of either the continuum or the particle nature of solvent alone. Further studies with different molecular systems, however, should be carried out to obtain more information on the molecular and hydrodynamic contributions to diffusion.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: tcc.chan@polyu.edu.hk.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors thank S. H. Lam, S. T. Chan, and W. K. Tang for their technical assistance. This work was supported in part by the Research Committee of the Hong Kong Polytechnic University under Grant No. 5-ZJF1. The authors are grateful to Professor W. T. Wong for help and discussions.

## REFERENCES

- (1) Tyrrell, H. J. V.; Harris, K. R. *Diffusion in Liquids*; Butterworths: London, 1984.
- (2) Zwanzig, R.; Harrison, A. K. Modifications of the Stokes-Einstein Formula. *J. Chem. Phys.* **1985**, *83*, 5861–5862.
- (3) Evans, D. F.; Chan, C.; Lamartine, B. C. The Effect of Charge upon Mobility. A Critical Examination of the Zwanzig Equation. *J. Am. Chem. Soc.* **1977**, *99*, 6492–6496.
- (4) Evans, D. F.; Tominaga, T.; Davis, H. T. Tracer Diffusion in Polyatomic Liquids. *J. Chem. Phys.* **1981**, *74*, 1298–1305.
- (5) Hiss, T. G.; Cussler, E. L. Diffusion in High Viscosity Liquids. *AIChE J.* **1973**, *19*, 698–703.
- (6) Kowert, B. A.; Dang, N. C. Diffusion of Dioxygen in *n*-Alkanes. *J. Phys. Chem. A* **1999**, *103*, 779–781.
- (7) Chen, S. H.; Davis, H. T.; Evans, D. F. Tracer Diffusion in Polyatomic Liquids. III. *J. Chem. Phys.* **1982**, *77*, 2540–2544.
- (8) Chen, S. H.; Evans, D. F.; Davis, H. T. Tracer Diffusion in Methanol, 1-Butanol and 1-Octanol from 298 to 433 K. *AIChE J.* **1983**, *29*, 640–645.
- (9) Pollack, G. L.; Enyeart, J. J. Atomic Test of the Stokes-Einstein Law. II. Diffusion of Xe through Liquid Hydrocarbons. *Phys. Rev. A* **1985**, *31*, 980–984.
- (10) Pollack, G. L.; Kennan, R. P.; Himm, J. F.; Stump, D. R. Diffusion of Xenon in Liquid Alkanes: Temperature Dependence Measurements with a New Method. Stokes-Einstein and Hard Sphere Theories. *J. Chem. Phys.* **1990**, *92*, 625–630.
- (11) Ould-Kaddour, F.; Barrat, J.-L. Molecular-Dynamics Investigation of Tracer Diffusion in a Simple Liquid. *Phys. Rev. A* **1992**, *45*, 2308–2314.
- (12) Kumar, S. K.; Szamel, G.; Douglas, J. F. Nature of the Breakdown in the Stokes-Einstein Relationship in a Hard Sphere Fluid. *J. Chem. Phys.* **2006**, *124*, 214501-1–214501-6.
- (13) Walser, R.; Mark, A. E.; van Gunsteren, W. F. On the Validity of Stokes' Law at the Molecular Level. *Chem. Phys. Lett.* **1999**, *303*, 583–586.
- (14) Walser, R.; Hess, B.; Mark, A. E.; van Gunsteren, W. F. Further Investigation on the Validity of Stokes-Einstein Behaviour at the Molecular Level. *Chem. Phys. Lett.* **2001**, *334*, 337–342.
- (15) Harris, K. R. The Fractional Stokes-Einstein Equation: Application to Water. *J. Chem. Phys.* **2010**, *132*, 231103-1–231103-3.
- (16) Harris, K. R. The Fractional Stokes-Einstein Equation: Application to Lennard-Jones, Molecular, and Ionic Liquids. *J. Chem. Phys.* **2009**, *131*, 054503-1–054503-8.
- (17) Matthiesen, J.; Smith, R. S.; Kay, B. D. Probing the Mobility of Supercooled Liquid 3-Methylpentane at Temperatures near the Glass Transition Using Rare Gas Permeation. *J. Chem. Phys.* **2012**, *137*, 064509-1–064509-8.
- (18) Rajian, J. R.; Huang, W.; Richert, R.; Quitevis, E. L. Enhanced Translational Diffusion of Rubrene in Sucrose Benzoate. *J. Chem. Phys.* **2006**, *124*, 014510-1–014510-8.
- (19) Rajian, J. R.; Quitevis, E. L. Translational Diffusion in Sucrose Benzoate near the Glass Transition: Probe Size Dependence in the Breakdown of the Stokes-Einstein Equation. *J. Chem. Phys.* **2007**, *126*, 224506-1–224506-10.
- (20) Su, J. T.; Duncan, P. B.; Momaya, A.; Jutila, A.; Needham, D. The Effect of Hydrogen Bonding on the Diffusion of Water in *n*-Alkanes and *n*-Alcohols Measured with a Novel Single Microdroplet Method. *J. Chem. Phys.* **2010**, *132*, 044506-1–044506-8.
- (21) Harris, K. R. Relations between the Fractional Stokes-Einstein and Nernst-Einstein Equations and Velocity Correlation Coefficients

in Ionic Liquids and Molten Salts. *J. Phys. Chem. B* **2010**, *114*, 9572–9577.

(22) Liu, H.; Maginn, E. A Molecular Dynamics Investigation of the Structural and Dynamic Properties of the Ionic Liquid 1-*n*-Butyl-3-Methylimidazolium Bis(Trifluoromethanesulfonyl)imide. *J. Chem. Phys.* **2011**, *135*, 124507-1–124507-16.

(23) Harris, K. R.; Kanakubo, M.; Tsuchihashi, N.; Ibuki, K.; Ueno, M. Effect of Pressure on the Transport Properties of Ionic Liquids: 1-Alkyl-3-methylimidazolium Salts. *J. Phys. Chem. B* **2008**, *112*, 9830–9840.

(24) Turton, D. A.; Corsaro, C.; Martin, D. F.; Mallamace, F.; Wynne, K. The Dynamic Crossover in Water Does Not Require Bulk Water. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8067–8073.

(25) Spohr, H. V.; Patey, G. N. Structural and Dynamical Properties of Ionic Liquids: The Influence of Ion Size Disparity. *J. Chem. Phys.* **2008**, *129*, 064517-1–064517-8.

(26) Kowert, B. A.; Sobush, K. T.; Fuqua, C. F.; Mapes, C. L.; Jones, J. B.; Zahm, J. A. Size-Dependent Diffusion in the *n*-Alkanes. *J. Phys. Chem. A* **2003**, *107*, 4790–4795.

(27) Chauhan, A. S.; Ravi, R.; Chhabra, R. P. Self-Diffusion in Liquid Metals. *Chem. Phys.* **2000**, *252*, 227–236.

(28) Mapes, M. K.; Swallen, S. F.; Ediger, M. D. Self-Diffusion of Supercooled *o*-Terphenyl near the Glass Transition Temperature. *J. Phys. Chem. B* **2006**, *110*, 507–511.

(29) Chung, S. H.; Lopato, R.; Greenbaum, S. G.; Shiota, H.; Castner, E. W., Jr.; Wishart, J. F. Nuclear Magnetic Resonance Study of the Dynamics of Imidazolium Ionic Liquids with  $-\text{CH}_2\text{Si}(\text{CH}_3)_3$  vs  $-\text{CH}_2\text{C}(\text{CH}_3)_3$  Substituents. *J. Phys. Chem. B* **2007**, *111*, 4885–4893.

(30) Macanita, A. L.; Zachariasse, K. A. Viscosity Dependence of Intramolecular Excimer Formation with 1,5-Bis(1-pyrenylcarboxy)-pentane in Alkane Solvents as a Function of Temperature. *J. Phys. Chem. A* **2011**, *115*, 3183–3195.

(31) Das, S. K.; Sahu, P. K.; Sarkar, M. Diffusion-Viscosity Decoupling in Solute Rotation and Solvent Relaxation of Coumarin 153 in Ionic Liquids Containing Fluoroalkylphosphate (FAP) Anion: A Thermophysical and Photophysical Study. *J. Phys. Chem. B* **2013**, *117*, 636–647.

(32) Evans, D. F.; Tominaga, T.; Chan, C. Diffusion of Symmetrical and Spherical Solutes in Protic, Aprotic, and Hydrocarbon Solvents. *J. Solution Chem.* **1979**, *8*, 461–478.

(33) Bagchi, B.; Bhattacharyya, S. Mode Coupling Theory Approach to the Liquid-State Dynamics. *Adv. Chem. Phys.* **2001**, *116*, 67–221.

(34) Bhattacharyya, S.; Bagchi, B. Decoupling of Tracer Diffusion from Viscosity in a Supercooled Liquid near the Glass Transition. *J. Chem. Phys.* **1997**, *107*, 5852–5862.

(35) Bhattacharyya, S.; Bagchi, B. Anomalous Diffusion of Small Particles in Dense Liquids. *J. Chem. Phys.* **1997**, *106*, 1757–1763.

(36) Ali, S. M.; Samanta, A.; Ghosh, S. K. Mode Coupling Theory of Self and Cross Diffusivity in a Binary Fluid Mixture: Application to Lennard-Jones Systems. *J. Chem. Phys.* **2001**, *114*, 10419–10429.

(37) Chan, T. C.; Tang, W. K. Diffusion of Aromatic Compounds in Nonaqueous Solvents: A Study of Solute, Solvent, and Temperature Dependences. *J. Chem. Phys.* **2013**, *138*, 224503-1–224503-15.

(38) Hildebrand, J. H. Motions of Molecules in Liquids: Viscosity and Diffusivity. *Science* **1971**, *174*, 490–493.

(39) March, N. H. Self-Diffusion Related to Shear Viscosity at the Melting Temperature of Metals. *J. Chem. Phys.* **1984**, *80*, 5345.

(40) Whitman, J. R.; Aranovich, G. L.; Donohue, M. D. Thermodynamic Driving Force for Diffusion: Comparison between Theory and Simulation. *J. Chem. Phys.* **2011**, *134*, 094303-1–094303-7.

(41) Vasanthi, R.; Bhattacharyya, S.; Bagchi, B. Anisotropic Diffusion of Spheroids in Liquids: Slow Orientational Relaxation of the Oblates. *J. Chem. Phys.* **2002**, *116*, 1092–1096.

(42) Lu, J. G.; Kong, R.; Chan, T. C. Effects of Molecular Association on Mutual Diffusion: A Study of Hydrogen Bonding in Dilute Solutions. *J. Chem. Phys.* **1999**, *110*, 3003–3008.

(43) Taylor, G. Dispersion of Soluble Matter in Solvent Flowing Slowly through a Tube. *Proc. R. Soc. London, Ser. A* **1953**, *219*, 186–203.

(44) Grushka, E.; Kikta, E. J., Jr. Diffusion in Liquids. II. The Dependence of the Diffusion Coefficients on Molecular Weight and on Temperature. *J. Am. Chem. Soc.* **1976**, *98*, 643–648.

(45) Chan, T. C.; Ma, N. L.; Chen, N. The Effects of Molecular Association on Mutual Diffusion in Acetone. *J. Chem. Phys.* **1997**, *107*, 1890–1895.

(46) Chan, T. C. Diffusion of Pseudospherical Molecules: An Investigation on the Effects of Dipole Moment. *J. Chem. Phys.* **1983**, *79*, 3591–3593.

(47) Anderson, D. K.; Babb, A. L. Mutual Diffusion in Non-ideal Liquid Mixtures. IV. Methanol-Carbon Tetrachloride and Dilute Ethanol-Carbon Tetrachloride Solutions. *J. Phys. Chem.* **1963**, *67*, 1362–1363.

(48) Collings, A. F.; Mills, R. Temperature-Dependence of Self-Diffusion for Benzene and Carbon Tetrachloride. *Trans. Faraday Soc.* **1970**, *66*, 2761–2766.

(49) Carman, P. C.; Miller, L. Self-Diffusion in Mixtures. Part 3. Nitromethane + Carbon Tetrachloride System. *Trans. Faraday Soc.* **1959**, *55*, 1838–1843.

(50) Kulkarni, M. V.; Allen, G. F.; Lyons, P. A. Diffusion in Carbon Tetrachloride-Cyclohexane Solutions. *J. Phys. Chem.* **1965**, *69*, 2491–2493.

(51) Chen, S. H.; Davis, H. T.; Evans, D. F. Tracer Diffusion in Polyatomic Liquids. II. *J. Chem. Phys.* **1981**, *75*, 1422–1426.

(52) Caldwell, C. S.; Babb, A. L. Diffusion in Ideal Binary Liquid Mixtures. *J. Phys. Chem.* **1956**, *60*, 51–56.

(53) Anderson, D. K.; Hall, J. R.; Babb, A. L. Mutual Diffusion in Non-ideal Binary Liquid Mixtures. *J. Phys. Chem.* **1958**, *62*, 404–408.

(54) Bidlack, D. L.; Kett, T. K.; Kelly, C. M.; Anderson, D. K. Diffusion in the Solvents Hexane and Carbon Tetrachloride. *J. Chem. Eng. Data* **1969**, *14*, 342–343.

(55) Easteal, A. J.; Woolf, L. A. Solute-Solvent Interaction Effects on Tracer Diffusion Coefficients. *J. Chem. Soc. Faraday Trans. 1* **1984**, *80*, 1287–1295.

(56) Edward, J. T. Molecular Volumes and the Stokes-Einstein Equation. *J. Chem. Educ.* **1970**, *47*, 261–270.

(57) Sun, C. K. J.; Chen, S. H. Tracer Diffusion of Aromatic Hydrocarbons in Liquid Cyclohexane up to Its Critical Temperature. *AIChE J.* **1985**, *31*, 1510–1515.

(58) Chan, T. C.; Chan, M. L. Diffusion of Pseudo-planar Molecules: An Experimental Evaluation of the Molecular Effects on Diffusion. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2371–2374.

(59) Chan, T. C.; Chen, N.; Lu, J. G. Diffusion of Disubstituted Aromatic Compounds in Ethanol. *J. Phys. Chem. A* **1998**, *102*, 9087–9090.

(60) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.

(61) CRC *Handbook of Chemistry and Physics*, 92nd ed.; Haynes, W. M., Lide, D. R., Eds.; CRC Press: Boca Raton, FL, 2011.