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Diffusion of aromatic compounds in nonaqueous solvents: A study of solute, solvent, and temperature dependences

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Tracer diffusivities (limiting mutual diffusion coefficients) of nonassociated aromatic compounds in *n*-hexane and cyclohexane have been measured at 298.2 K by Taylor's dispersion method. These new data, together with other diffusivities of nonassociated pseudoplanar solutes reported in the literature, are used to determine the separate effects of solute and solvent on tracer diffusion. The data show that for a given pseudoplanar solute diffusing in different solvents at 298.2 K, the tracer diffusivity is dependent not only on the fractional viscosity of the solvent but also on a function of the solvent's molar density, molecular mass, and free volume fraction. For different pseudoplanar aromatic solutes diffusing in a particular solvent at a constant temperature, there is a linear relationship between the reciprocal of the tracer diffusivity and the molecular volume of the solutes. The results are discussed in respect to relevant theories and experimental studies in the literature. An idealized relation, developed on the basis of the Einstein equation by incorporating the newly found solute and solvent dependences, is capable of describing a total of 176 diffusivities of nonassociated pseudoplanar solutes in various solvents at different temperatures to within an average error of ±2.8%. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4808216]

I. INTRODUCTION

Diffusion has long been a subject of research interest because of its importance in biological systems, chemical reactions, and processing technologies. Although extensive studies on diffusion have been done over the past few decades with considerable progresses, our knowledge on diffusion at the molecular level is still quite limited. In particular, there is a lack of general theories that can satisfactorily describe the diffusion behavior of a wide range of molecules in dense fluids. This may be attributed partly to the complexity of the dynamics involved in the diffusion process and partly to the insufficient amount of reliable diffusion data in the literature for systematic studies.

There have been two major approaches in the study of diffusion in molecular liquids. Traditionally, diffusivities (diffusion coefficients) of liquid molecules have been understood in terms of the hydrodynamic theory, often using the well-known Stokes-Einstein (SE) relation. For limiting mutual diffusion (diffusion at trace concentration of solute), the SE relation describes diffusivity D_{12} by the expression

$$D_{12} = \frac{k_B T}{6\pi r_1 \eta}, \qquad (1)$$

where k_B is the Boltzmann constant, T refers to the absolute temperature, r_1 is the radius of the solute, and η represents the viscosity of the solvent. While the SE relation can predict diffusivities of large spherical solutes reasonably well, it nevertheless fails for solutes small in size compared to solvent molecules.[1–3] Invalidity of the SE relation has also been

found in computer simulations and theoretical studies.[4–7] Although many modified SE relations have been developed, it appears insofar that none could satisfactorily account for a broad range of diffusivities. The SE relation and its modifications have been reviewed by Cussler[8] and Reid *et al.*[9]

The other major approach in diffusion study is Enskog's kinetic theory, which takes binary collisions of molecules into account. The rough-hard-sphere (RHS) model[10] is a typical representation of this approach. This model is based on the van der Waals (VDW) picture of condensed matter, which assumes that motions of molecules in a liquid are determined primarily by the short-range repulsive intermolecular forces (i.e., the size and shape of molecules), while weak dipole-dipole interactions and other attractive forces that vary slowly in space play only a minor role. The VDW picture has been reviewed by Chandler *et al.*[11] The RHS model relates tracer diffusivity D_{12} by the equation[12–14]

$$D_{12} = \frac{3 (k_B T)^{1/2}}{2n_2 (\sigma_1 + \sigma_2)^2} \left(\frac{1}{2\pi\mu}\right)^{1/2} \frac{A_{12}}{g_{12}} \left(\frac{D_{SHS}}{D_E}\right), \qquad (2)$$

where n_2 is the number density of the solvent, σ_1 and σ_2 represent the molecular diameters of the solute and solvent, respectively, μ is the reduced mass of solute and solvent molecules, A_{12} refers to the translation-rotation coupling constant, g_{12} represents the unlike radial-distribution function at contact, and (D_{SHS}/D_E) is the computed correction to the Enskog theory to take into account of the correlated molecular motions. In Eq. (2), however, the physical significance of the computed correction (D_{SHS}/D_E) term has never been very clear, and there have been considerable disagreements about the translation-rotation coupling constant, A_{12}, in the literature.[2, 15–18] Furthermore, it is well recognized that the

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kinetic theory generally overestimates the mass effect on diffusion.[19,20] Details of the RHS model and the kinetic theory for diffusion have been discussed by Tyrrell and Harris.[21]

The hydrodynamic theory basically describes mutual diffusion as a solute moving in a continuum of solvent, whereas the kinetic theory considers solute and solvent molecules as discrete particles travelling with collisions in the diffusion process. In recent years, molecular dynamic (MD) simulations[22(a)–22(h)] and mode-coupling theory (MCT)[19,20,23–26] as well as other theoretical methods[27] have also been widely used in the study of diffusion. Nonetheless, it appears that not many of the recent theoretical treatments could demonstrate good validation of their results by experimental facts.

New experimental measurements designed to allow systematic investigation and to give useful information on the diffusion behavior of molecules in liquids are currently few in the literature. In this laboratory, we have long been interested in experimental studies of various molecular effects on mutual diffusion in liquids. Previously, we have reported the effects of molecular mass,[28,29] dipole moment,[28,29] shape,[29,30] and size[30,31] of solutes on diffusivities. Investigations of the effects of hydrogen-bonding[31–35] and the steric effects[36] of associated molecules on diffusion have also been published. In this work, we report new tracer diffusivities of some aromatic compounds in *n*-hexane and cyclohexane at 298.2 K. It should be noted that throughout this study the term tracer diffusivity refers to mutual diffusion coefficient of a solute at trace (very dilute) concentration in a molecular liquid, i.e., limiting mutual diffusion coefficient. The solutes chosen in this study are pseudoplanar (disclike) molecules that are nonassociated in organic solvents, and they are all similar in chemical nature. For nonspherical molecules, the diffusion in liquids is anisotropic.[22(h)] To minimize the different effects of translation-rotation coupling due to differences in shape, all disc-shaped solutes used in this work are very thin molecules with small aspect ratio values. The newly measured data and those reported previously in the literature are utilized to ascertain the solute and solvent dependences of diffusivities. These dependences are then combined to build a more generalized relation for describing the diffusivities of nonassociated pseudoplanar solutes in liquids. The model constructed is based primarily on the SE relation, with the Stokes law being replaced by the combination of solute and solvent dependences. It is then tested by fitting all experimental data at different temperatures.

II. EXPERIMENT

Limiting mutual diffusion coefficients (tracer diffusivities) were measured by using the Taylor dispersion method, also known as the chromatographic peak-broadening technique. In this method, a small sample of a solution at dilute concentration is injected into a pure solvent flowing in a capillary tube. Taylor[37] has shown that the combination of flow and diffusion results in a Gaussian distribution of solute along the tube, provided that the flow is laminar. The diffusion coefficient at trace concentration can be determined by the relation[38]

$$D_{12} = 0.2310 R^2 t_r / \left(W_{1/2} \right)^2, \tag{3}$$

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

The apparatus used for the measurements here was similar in design to that reported in Refs. 35 and 36. In this work, however, the detector was a differential refractometer (Shimadzu model RID-10A). To improve the required condition of laminar flow, the diffusion tube was changed to a 91.4 m length of 304 stainless steel tube with a smaller 0.762 mm i.d. (Supelco). The tube (of 1.59 mm o.d.) was coiled into a circle with a diameter of about 23 cm. The solvent was delivered by an Agilent HPLC pump (model 1100) with a flow rate precision of ±0.5%. In the experiment, a small sample of 20-50 μl was injected into a stream of solvent in the diffusion tube. The coiled capillary tube was mounted horizontally and immersed in a constant-temperature bath (Julabo model FP45) controlled to within ±0.01 K. Temperatures were measured by a certified thermometer (Baird and Tatlock, No. GDZ27736). To ensure laminar flow, the solvent flow rate was adjusted so that the constant volume flow was between 0.10 and 0.16 ml/min. At the end of the diffusion tube, the solute dispersion peak was detected by the differential refractometer. At least three measurements were made to obtain a diffusion coefficient.

In this study, the solvents cyclohexane (99.9%+, Aldrich), *n*-hexane (99%+, Aldrich), and 1-butanol (99.8%, Aldrich) were degassed by ultrasonic bath and then filtered before use with a 20 μm stainless-steel solvent filter. The solute mesitylene (98%, Riedel-de Haën) was purified by fractional distillation; benzene (99.9%+, Aldrich), toluene (99.5%, E. Merck), chlorobenzene (99.9%+, Aldrich), ethylbenzene (99%+, BDH), naphthalene (99%,BDH), 1,2,4-trichlorobenzene (99%+, Aldrich), *n*-propylbenzene (99%, E. Merck), biphenyl (99%+, Koch-Light), 1,2,4-trimethylbenzene (99%+, Aldrich), and hexamethylbenzene (99%+, Aldrich) were used as received. To test our apparatus, we have carried out a few measurements of diffusivities against previously reported data, and have generally obtained good agreement within experimental error.

III. RESULTS AND DISCUSSION

The measured diffusion coefficients (D_{12}) are presented in Table I. These values are the averages resulting from three or more diffusion measurements. The uncertainty listed is the average absolute error. The reproducibility of data here is consistent with those reported in our previous works[33–36] using basically the same technique. In this study, we also report the tracer diffusivities of 1,2,4-trichlorobenzene and mesitylene in 1-butanol, which at 298.15 K are 0.730 ± 0.009 and 0.732 ± 0.008 × 10^{-9} m² s⁻¹, respectively. These diffusion coefficients, not listed in Table I, were measured mainly to verify the insensitivity of tracer diffusivity to solute mass as found in some previous studies.[28–30] Mesitylene and 1,2,4 -trichlorobenzene are two molecules

TABLE I. Limiting mutual diffusion coefficients (D_{12}/ 10^{-9}m^2 s^{-1}) in n-hexane and cyclohexane at 298.15 K.[a]

| Solute	V_1 (Å^3)[b]	Solvent	
		n-Hexane	Cyclohexane
Benzene	81.1	4.72 ± 0.04 (4.74)[c]	(1.89)[d]
Chlorobenzene	97.2	4.22 ± 0.04	1.71 ± 0.02
Toluene	97.6	(4.30)[e]	1.71 ± 0.02
			(1.728 ± 0.007)[f]
Bromobenzene	102.8	(3.86 ± 0.04)[g]	…
Ethylbenzene	113.8	3.94 ± 0.04	1.56 ± 0.02
p-Xylene	114.2	…	(1.645 ± 0.002)[f]
Naphthalene	125.4	3.76 ± 0.03	1.44 ± 0.01
			(1.452 ± 0.005)[f]
1,2,4-Trichlorobenzene	129.3	3.50 ± 0.04	1.39 ± 0.01
Propylbenzene	130.0	3.60 ± 0.04	1.41 ± 0.02
1,2,4-Trimethylbenzene	130.7	3.57 ± 0.03	…
Mesitylene	130.7	3.54 ± 0.03	1.40 ± 0.01
			(1.400 ± 0.009)[f]
Biphenyl	152.4	3.29 ± 0.03	1.28 ± 0.02
Anthracene	169.7	(3.09)[h]	…
Phenanthrene	169.7	(3.08)[i]	(1.199 ± 0.002)[f]
Hexamethylbenzene	180.3	…	1.09 ± 0.01
Pyrene	187.0	(2.86)[h]	…

[a]Literature values are in parentheses.
[b]The values of van der Waals volumes are averages from Refs. 39–42.
[c]Average value from Refs. 43–46.
[d]Average value from Refs. 44, 45, 51, and 52.
[e]Average value from Refs. 47 and 48.
[f]From Ref. 51.
[g]From Ref. 46.
[h]Average value of data in Ref. 49.
[i]From Ref. 50.

similar in shape but different in molecular mass by about 51%. These two diffusion data are also useful for the investigation of solvent dependence of tracer diffusivities (see Sec. III B). It should be noted that 1-butanol is a solvent of relatively higher viscosity than most other solvents in the present study. Table I also includes some literature values of tracer diffusivities of nonassociated aromatic solutes. Wherever comparisons are available, our data and the literature values are in good agreement within experimental errors. Also shown in this table are values of the VDW volume of the solute molecules, which are calculated from group increments.[39–42]

A. Solute dependence

All aromatic solutes in this work are pseudoplanar (thin disc-shaped) in structure and nonassociated in the solvents studied. The values of aspect ratio of these thin disclike molecules are approximately between 0.25 and 0.4 only, except for rubrene and pyrene with values slightly less than 0.25. The effect of translation-rotation coupling on diffusion of oblate solutes (with different values of aspect ratio) in a solvent has been studied by Visanthi *et al.*[22(h)] using the method of MD simulations. The results there show that both the orientation relaxation time τ_{2R} and the product $D_T\tau_{2R}$, where D_T is the total translation diffusion coefficient, are fairly independent of the aspect ratio of the disclike solute molecules which are of values between 0.25 and 0.5. This implies that the ef-
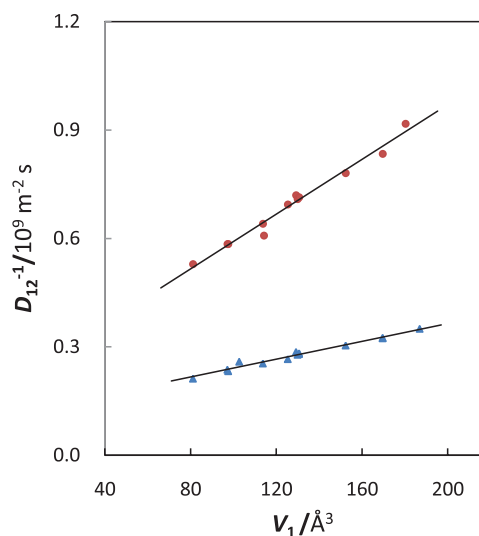
FIG. 1. Variation of $1/D_{12}$ with the molecular volume of solutes diffusing in cyclohexane (●) and n-hexane (▲) at 298.2 K.

fects of solute shape or translation-rotation coupling on diffusion in a given solvent are approximately equal for disclike solutes within this range of aspect ratios. Although there is no data available for solutes with aspect ratio below 0.25, the effects for rubrene and pyrene are nonetheless not expected to deviate significantly from those of other solutes in this work, as it has been pointed out in the MD simulation study[22(h)] that the orientation relaxation time depends only weakly on aspect ratio less than 0.3. Hence, for all pseudoplanar solutes in this work, the effects of translation-rotation coupling on diffusion in a given solvent should generally be about the same and not significantly affected by the very small differences in the shape of the solutes studied.

For the solutes in n-hexane and cyclohexane at 298.2 K, there exists a linear dependence of the reciprocal of the diffusivities ($1/D_{12}$) on the VDW volume (V_1) of the solutes. The relationship can be expressed by the equation

$$D_{12}^{-1}/10^9\text{m}^{-2}\text{s} = aV_1/\text{Å}^3 + b,\qquad(4)$$

where a and b are constants. The linear regression lines for data in Table I are displayed in Fig. 1. The present results are consistent with those found previously on the diffusivities of similar solutes in other solvents.[30, 32–35] The constants a and b for systems in this and previous works, together with their respective correlation coefficients and average % deviations of fit, are given in Table II. It is noteworthy that Eq. (4) is independent of solute mass. This can be verified by comparing the data for chlorobenzene and toluene as well as 1,2,4-trimethylbenzene, mesitylene, and 1,2,4-trichlorobenzene in Table I, in addition to the two solutes in 1-butanol mentioned above. More evidences of the insignificance of solute mass on tracer diffusion have been reported in Refs. 28–30. The above experimental results are in agreement with the MCT study of Bhattacharyya and Bagchi,[25(b)] which found that the effect of solute mass on diffusion is generally quite weak; in particular, the solute-mass dependence can normally be considered as negligibly small when changes of solute mass are small within a factor of 2 or so. It should be pointed out that it

TABLE II. Parameters and statistics of linear regressions using Eq. (4).

Solvent	Temperature (K)	Source of data	No. of data	Intercept ($a/10^{-1}$)	Slope ($b/10^{-3}$)	Correlation coefficient	Average deviation (%)
Acetone	298.2	Ref. 30	9	1.465	1.264	0.987	1.36
Cyclohexane	298.2	This work	12	2.129	3.787	0.990	1.66
	333.2	Ref. 51	6	1.571	1.873	0.979	2.34
Ethanol	298.2	Ref. 30	9	1.907	4.440	0.993	1.49
	313.2	Ref. 53	5	1.878	3.044	0.996	1.39
n-Hexane	273.2	Ref. 14	6	1.612	1.631	0.979	2.36
	298.2	This work	14	1.177	1.233	0.988	1.62
	299.2	Ref. 14	6	1.101	1.268	0.976	2.57
	313.2	Ref. 14	7	0.836	1.177	0.999	1.69
	333.2	Ref. 54	6	0.694	0.924	0.991	1.36
	333.2	Ref. 14	5	0.634	0.991	0.999	1.02
Methanol	298.2	Ref. 35	9	1.925	2.296	0.997	0.78
n-Tetradecane	298.2	Ref. 30	8	3.424	6.229	0.986	1.22

is rare for real molecules, except hydrogen, to have the same size but different masses by more than a factor of 2.

The linear relationship between $1/D_{12}$ and V_1 for nonassociated pseudoplanar solutes is not limited to 298.2 K only. Dymond[14] has measured D_{12} of aromatic compounds at trace concentration in n-hexane at different temperatures from 273.2 K to 333.2 K. Sun and Chen[51,53,54] have reported tracer diffusivities of nonassociated aromatic solutes in cyclohexane, ethanol, and n-hexane at temperatures above 298.2 K. We have carried out linear regressions for their data at temperatures below the normal boiling point of solvent (but excluding those data at higher temperatures which were measured at different pressures above 1 atm). All data, except one of Dymond's[14] at 299.2 K, have been found to follow Eq. (4) very closely. The results are shown in Fig. 2 and in Table II. It is noteworthy that the straight lines fit remarkably well all Dymond's data at 313.2 K and 333.2 K from a small benzene ($V_1 = 81.1$ Å^3) to a very large rubrene molecule ($V_1 = 509.1$ Å^3).

In view of the correlation coefficients and the average % deviations for the 13 sets of linear regressions in Table II, it is clear that Eq. (4) can correctly represent the solute dependence of D_{12} in any given solvent at constant temperature, at least for the range of pseudoplanar solutes in this study. This solute dependence of Eq. (4) is nonetheless not quite consistent with that predicted by the SE relation in which D_{12} is inversely proportional to r_1 (or $V_1^{1/3}$) of solutes. To improve the solute dependence in the SE relation, an "effective hydrodynamic radius" has been suggested by Zwanzig and Harrison[55] to replace the van der Waals' radius r_1 for each solute in a solvent. It is not known if this correction has any relationship with Eq. (4) in the present study; however, the forms of the equations for solute dependence are still different.

It is of interest to compare Eq. (4) with the solute dependence in the RHS theory. For aromatic solutes with the same shape diffusing in a particular solvent at constant temperature, Eq. (2) can be reduced to

$$D_{12} \propto \frac{D_{SHS}/D_E}{(\sigma_1 + \sigma_2)^2 \mu^{1/2} g_{12}}, \quad (5)$$

since the translation-rotation coupling constant, A_{12}, in the RHS theory is dependent on the shape of the colliding molecules only.[10] In a given solvent, the computed correction to the Enskog theory, D_{SHS}/D_E, depends only on the size and mass of the solutes. By taking into consideration the experimental evidences[28–30] on the insensitivity of tracer diffusivities to solute mass, we have previously shown[30]

$$D_{12} = \frac{D_{SHS}^\sigma/D_E^\sigma}{(\sigma_1 + \sigma_2)^2 g_{12}}, \quad (6)$$

where $D_{SHS}^\sigma/D_E^\sigma$ is a function of σ_1 only that can be represented by a polynomial or quadratic equation in $1/\sigma_1$. Using the g_{12} expression suggested by Chen $et\ al.$,[56] the unlike-radial distribution function at contact for tracer diffusion in a particular solvent can be simplified to

$$g_{12} = \frac{(c_2\sigma_1^2 + c_1\sigma_1 + c_0)}{\sigma_1 + \sigma_2}, \quad (7)$$

where c_2, c_1, and c_0 are constants of the solvent. From Eqs. (6) and (7), one can obtain

$$D_{12} \propto \frac{1}{\sum_{i=0}^{n} k_i\sigma_1^i}, \quad (8)$$

where k_i's are constants. Since V_1 is the solute volume proportional to σ_1^3 and if $D_{SHS}^\sigma/D_E^\sigma$ can be given by a quadratic equation in $1/\sigma_1$, it can be shown from Eqs. (6)–(8) that

$$D_{12} \propto \frac{1}{k_3 V_1 + k_2 V_1^{2/3} + k_1 V_1^{1/3} + k_0}. \quad (9)$$

Alternatively, Eq. (9) can be rewritten as

$$1/D_{12} = h_3 V_1 + h_2 V_1^{2/3} + h_1 V_1^{1/3} + h_0, \quad (10)$$

where h_3, h_2, h_1, and h_0 are constants. In respect to this relation, our experimental result of Eq. (4) for the solute dependence of tracer diffusion appears to be partly related to but not exactly the same in form as Eq. (10) which has been approximated from the RHS model. Equations (4) and (10) are consistent, however, if the sum $(h_2 V_1^{2/3} + h_1 V_1^{1/3} + h_0)$ is constant, i.e., if changes in solute volume can only cause very small or insignificant variation in this quantity as compared to $h_3 V_1$. This could happen, for example, when the values of h_2
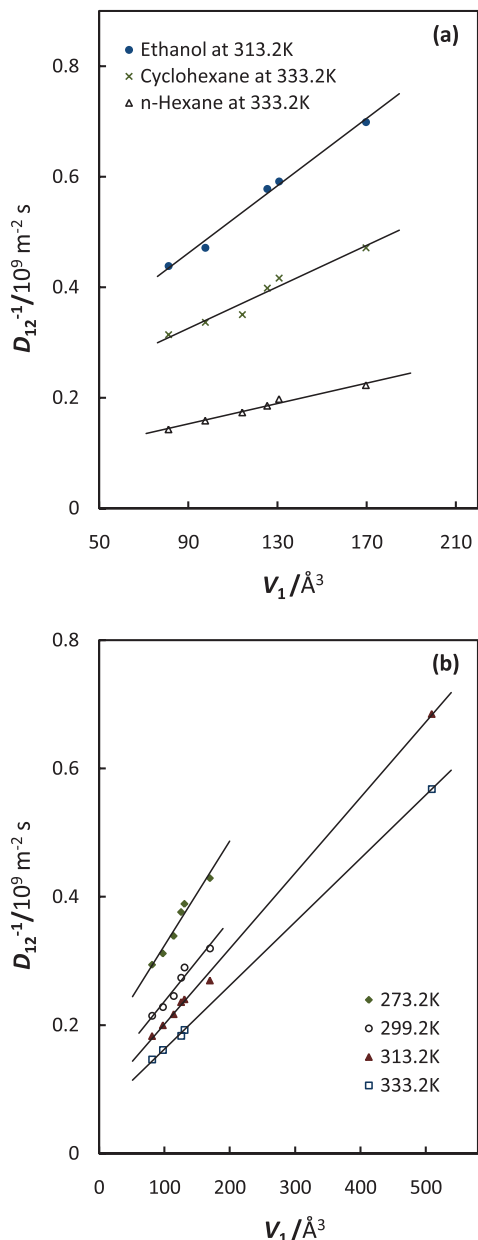
FIG. 2. Plot of $1/D_{12}$ vs V_1 at different temperatures. (a) Diffusivities from Refs. 51, 53, and 54; (b) *n*-hexane data from Ref. 14.

and h_1 are either small or of opposite signs or if the range of solute sizes is not too wide (since V_1 is larger than $V_1^{2/3}$ and $V_1^{1/3}$). Whether the RHS theory can be validated by experimental results or not, however, awaits further investigations. Nonetheless, it should be pointed out that the linear relationship in Eq. (4) between $1/D_{12}$ and V_1 may not necessarily exist for an extremely wide range of solute sizes (in particular, those of virtual model molecules in computer studies) and for solutes with different shapes. Equation (4), however, should be valid for solutes of normal size that the SE relation is inapplicable.

B. Solvent dependence

For tracer diffusion of a given solute in different solvents, the SE relation predicts that diffusivity is inversely pro-

portional to the viscosity of the solvent. Except for macromolecules, however, numerous experimental studies[3,57–66] have shown that tracer diffusivity is inversely proportional to a fractional power of the viscosity of the solvent instead. This fractional power dependence of viscosity on diffusion is often referred to in the literature as the fractional Stokes-Einstein (FSE) relation, $(D_{12}/T) \propto \eta^{-t}$, where t is known to be normally less than unity and generally around 2/3.[19,58] The FSE relation hence implies that the SE relation usually underestimates the diffusivities of solutes that are not very large as compared to solvent molecules. The enhanced diffusion has been explained by the so-called microviscosity effect, i.e., the viscosity around a small solute is different from the bulk viscosity of solvent.[67] Although Hiss and Cussler[58] have been able to rationalize the exponent of 2/3 on the basis of Eyring's absolute rate theory and Bagchi and Bhattacharyya[7,19] have indicated in their MCT studies that decoupling of the solute motion from the structural relaxation of the solvent could lead to fractional viscosity dependence, nonetheless, a quantitative theory of the FSE relation is still not yet available. Recently, however, there has been a great deal of interest[68–76] in the use of the FSE relation for the study of diffusion. One of our objectives in the present study is to critically test the applicability of the FSE relation against precise diffusion data. It is also our aim to ascertain the solvent dependence of tracer diffusivities of nonassociated aromatic solutes.

Table III shows the tracer diffusivities of pseudoplanar solutes in various solvents at 298.2 K. The data were mainly collected from different sources in the literature, in addition to the ones measured in this work. Only solutes with tracer diffusivities in at least six different solvents were included in the table for carrying out useful analysis on the solvent dependence. A total of 9 solutes ranging from benzene ($V_1 = 81.1$ Å^3) to biphenyl ($V_1 = 152.4$ Å^3) are listed in Table III.

At constant temperature, the FSE relation can be simplified to

$$D_{12}^{-1} \propto \eta^t, \qquad (11)$$

and can be expressed by the equation

$$\log D_{12}^{-1} = z_1 + t \log \eta, \qquad (12)$$

where z_1 is a constant. Viscosity η, density d, and other properties of the solvents concerned are given in Table IV. When the data for each solute are fitted to Eq. (12), a straight line with slope t is expected. Nonetheless, the 9 sets of data in the table can only be loosely fitted with Eq. (12).The average % deviations between the experimental and the calculated values of D_{12} are from 3.8% for 1, 2, 4- trichlorobenzene (with 6 data) to 9.7% for benzene (with 15 data). The maximum deviation for individual data (benzene in CCl$_4$) is 31.2%, and the overall average deviation for the 9 sets of data is 6.9%. It should be noted that a fairly large number (80 in total at 298.2 K) of data were used in the analysis. In view of the precisions of these experimental data from various sources, an average deviation of 6.9% is not quite satisfactory, especially when 7 out of the 80 calculated values deviate from the experimental data by more than 19%. The result in this study indicates that the FSE relation may not be adequate to

TABLE III. Experimental D_{12} values and calculated results for nonassociated aromatic solutes in various solvents at 298.15 K.

Solute (t, m, y) $[B]$	Solvent	D_{12} $(10^{-9} m^2 s^{-1})^a$	Refs.	Calc. D_{12} $(10^{-9} m^2 s^{-1})^b$
Benzene	Acetone	4.18	30, 45	4.15
(0.689, 0.718, 0.675)	Acetonitrile	3.81 ± 0.04	46	3.61
[0.404]	Benzene	2.247 ± 0.007^c	77	2.39
	Carbon tetrachloride	1.47	50, 78	1.56
	Chlorobenzene	1.86	43, 79	1.88
	Cyclohexane	1.89	44, 45, 51, 52	1.96
	n-Dodecane	1.547 ± 0.003	44	1.57
	Ethanol	1.79 ± 0.01	30	1.72
	n-Heptane	3.89	43, 48	3.89
	n-Hexadecane	0.898 ± 0.002	44	0.916
	n-Hexane	4.72 ± 0.04	This work	4.79
	Methanol	2.61 ± 0.02	35	2.66
	n-Octane	3.19	43, 79	3.19
	n-Tetradecane	1.18 ± 0.01	30	1.18
	Toluene	2.47	46, 48	2.55
Chlorobenzene	Acetone	3.71 ± 0.03	30	3.75
(0.707, 0.709, 0.647)	Benzene	2.084 ± 0.010	43	2.16
[0.439]	Bromobenzene	1.26 ± 0.01	78	1.22
	Chlorobenzene	1.758 ± 0.009^c	43	1.70
	Cyclohexane	1.71 ± 0.02	This work	1.77
	Ethanol	1.61 ± 0.01	30	1.55
	n-Hexane	4.22 ± 0.04	This work	4.33
	Methanol	2.40 ± 0.02	35	2.40
	n-Tetradecane	1.06 ± 0.01	30	1.06
	Toluene	2.21 ± 0.02	78	2.30
Toluene	Acetone	3.75 ± 0.03	30	3.74
(0.714, 0.732, 0.682)	Acetonitrile	3.38 ± 0.03	46	3.24
[0.442]	Carbon tetrachloride	1.404	80	1.40
	Chlorobenzene	1.69 ± 0.02	78	1.69
	Cyclohexane	1.71 ± 0.02	This work	1.77
	n-Decane	2.09 ± 0.04	81	2.01
	n-Dodecane	1.38 ± 0.03	81	1.42
	Ethanol	1.62 ± 0.02	30	1.55
	n-Heptane	3.72 ± 0.07	81	3.50
	n-Hexane	4.30	47, 48	4.32
	Methanol	2.42 ± 0.02	35	2.40
	n-Tetradecane	1.05	30, 81	1.06
	Toluene	2.24 ± 0.02^c	46	2.29
Ethylbenzene	Acetone	3.45 ± 0.02	30	3.40
(0.705, 0.727, 0.676)	Cyclohexane	1.56 ± 0.02	This work	1.61
[0.487]	Ethanol	1.45 ± 0.01	30	1.41
	n-Hexane	3.94 ± 0.04	This work	3.93
	Methanol	2.23 ± 0.01	35	2.18
	n-Tetradecane	0.953 ± 0.008	30	0.965
Naphthalene	Acetone	3.25 ± 0.03	30	3.20
(0.723, 0.734, 0.684)	Acetonitrile	2.74 ± 0.14	82	2.78
[0.523]	Carbon tetrachloride	1.200	80	1.20
	Cyclohexane	1.44 ± 0.01	This work	1.51
	Ethanol	1.32 ± 0.01	30	1.33
	n-Hexane	3.76 ± 0.03	This work	3.69
	Methanol	2.08 ± 0.02	35	2.05
	n-Tetradecane	0.889 ± 0.007	30	0.907
1,2,4-Trichlorobenzene	Acetone	3.13 ± 0.03	30	3.14
(0.711, 0.713, 0.666)	1-Butanol	0.730 ± 0.009	This work	0.713
[0.536]	Cyclohexane	1.39 ± 0.01	This work	1.48
	Ethanol	1.30 ± 0.01	34	1.30
	n-Hexane	3.50 ± 0.04	This work	3.62
	n-Tetradecane	0.832 ± 0.008	30	0.889

TABLE III. (*Continued.*)

Solute (t, m, y) [B]	Solvent	D_{12} (10^{-9}m^{2}s^{-1})[a]	Refs.	Calc. D_{12} (10^{-9}m^{2}s^{-1})[b]
n-Propylbenzene	Acetone	3.24 ± 0.03	30	3.13
(0.715, 0.737, 0.686)	Cyclohexane	1.41 ± 0.02	This work	1.48
[0.533]	Ethanol	1.32 ± 0.02	30	1.30
	n-Hexane	3.60 ± 0.04	This work	3.61
	Methanol	2.06 ± 0.01	35	2.00
	n-Tetradecane	0.871 ± 0.008	30	0.885
Mesitylene	Acetone	3.16 ± 0.03	33	3.11
(0.731, 0.706, 0.655)	1-Butanol	0.732 ± 0.008	This work	0.708
[0.522]	Carbon tetrachloride	1.193	80	1.17
	Cyclohexane	1.40 ± 0.01	This work	1.47
	Ethanol	1.32 ± 0.01	34	1.29
	n-Hexane	3.54 ± 0.03	This work	3.59
	Methanol	2.02 ± 0.01	35	2.00
Biphenyl	Acetone	2.89 ± 0.03	30	2.81
(0.717, 0.728, 0.679)	Acetonitrile	2.48 ± 0.12	82	2.44
[0.587]	Benzene	1.558	83	1.62
	Carbon tetrachloride	1.074	80	1.05
	Cyclohexane	1.28 ± 0.02	This work	1.33
	Ethanol	1.20 ± 0.01	34	1.16
	n-Hexane	3.29 ± 0.03	This work	3.24
	Methanol	1.85 ± 0.02	35	1.80
	n-Tetradecane	0.792 ± 0.009	30	0.795

[a]Average value where two or more references are given.
[b]Calculated from Eq. (31) with $p = 0.800$ and $q = 53.9$.
[c]Self diffusivity.

represent the solvent dependence of tracer diffusion, although the trend of the relation is correct. This is not unexpected, as diffusion is a complex process. In particular, solvent dependence should involve collective dynamics which probably cannot be sufficiently represented by a single variable η only.

It is of interest to discuss the values of the fractional power t found in this work as well as those reported in other studies. The values of the slope (exponent t) for the 9 sets of data are listed also in Table III. These values, from 0.689 for benzene to 0.731 for mesitylene, are in general quite close, although there appears vaguely a weak dependence of t on solute size (see Table III). The mean value of t in this study is 0.712, with an average error of ±0.008 or ±1.1% only. Individually, our t values of 0.723 for naphthalene and 0.717 for biphenyl agree well with the literature values[58,70] of 0.69 and 0.718, respectively. The values of 0.716 for benzene, 0.712 for *p*-terphenyl, 0.726 for *trans*-stilbene, and 0.749 for anthracene reported by Kowert *et al.*[71] as well as 0.722 for rubrene given by Quitevis *et al.*[75] are in very good agreement with our mean t value of 0.712 for the pseudoplanar solutes. It is noteworthy that rubrene is larger than benzene in size by more than 6 times, but that these two pseudoplanar aromatic compounds have similar t values. That the t values are not a strong function of solute size for solutes of the same chemical type has already been shown by Kowert *et al.*[76] in their diffusion study of the solutes 1-alkenes and *n*-alkanes with 6 or more carbon atoms. Closeness in t values in similarly shaped solutes has also been observed by Harris.[68] It should be noted, however, that t values in general may depend not only on the shape but probably to some extent on the size of solutes too if the range of solute size is considerably wide.

Nonetheless, among all aromatic compounds, benzene is already the smallest, and in real molecules very few aromatic compounds pseudoplanar in shape are larger than rubrene.

Notwithstanding all the aforesaid agreements about the t values, there are actually many discrepancies in the literature. For example, different values of 0.563,[3] 0.598,[71] 0.708,[64] and 0.941[68] have been reported for Xe; the values[49] of 0.943 (in *n*-alkanes) and 0.982 (in cyclohexane) for rubrene are very much different from that of 0.722 for the same solute.[75] Also, values of 0.717, 0.755, and 1.01 for CCl$_4$ as well as 0.472, 0.538, and 0.91 for CH$_4$ have been published.[3,68,71] These are just a few examples of the inconsistent or contradictory reports for the t values in the literature. As Harris[68] has recently pointed out, there are different ways to derive the t value. The value of exponent t may depend on the equations as well as units used, in addition to the accuracy of the data and number of data employed. Some authors have calculated t on the basis of isobaric and isothermal conditions, yet others have used data at different temperatures and under different pressures (thus densities) for the calculation. Without a standard state, however, comparisons of t values are probably not very meaningful.

All 80 data in this study of solvent dependence were measured at a standard state of 1 atm at 298.2 K, and Eq. (11) or its equivalent Eq. (12) was consistently used for the calculation of t. Also of importance was the fact that the data were collected from different sources, which allowed more statistically objective results. To overcome the deficiency of the solvent dependence of tracer diffusivities in terms of the fractional power of η only, we have searched the literature for relevant theories and studies that can be applied to extend the

TABLE IV. Values of η, M_2, d, ρ_2, V_2, and $\bar{V}_f/\bar{V}_m$ of solvents at different temperatures.

Temp.(K)	Solvent	η/cp[a]	M_2[b]	d (g cm^{-3})[c]	ρ_2 (10^{-3}mol cm^{-3})	V_2 (Å^3)[d]	$\bar{V}_f/\bar{V}_m$
273.15	n-Hexane	0.379	86.2	0.6772	7.858	107.5	0.4912
280.05	n-Heptane	0.478	100.20	0.6966[a]	6.952	123.7	0.4822
298.15	n-Hexadecane	3.063	226.44	0.7700	3.400	269.2	0.4487
	1-Butanol	2.534[e]	74.1	0.8057	10.870	83.3	0.4545
	n-Tetradecane	2.119[f]	198.34	0.7592	3.828	236.9	0.4540
	n-Dodecane	1.390	170.33	0.7452	4.375	204.5	0.4611
	Ethanol	1.057	46.1	0.7849[g]	17.038	51.0	0.4768
	Bromobenzene	1.038	157.01	1.4882[g]	9.478	102.8	0.4135
	Cyclohexane	0.901	84.2	0.7739	9.196	97.0	0.4627
	Carbon tetrachloride	0.900[f]	153.82	1.5844[g]	10.300	89.9	0.4424
	n-Decane	0.838[b]	142.3	0.7263[g]	5.105	172.2	0.4706
	Chlorobenzene	0.742[f]	112.56	1.1009[g]	9.781	97.2	0.4277
	Benzene	0.606	78.1	0.8736[g]	11.184	81.1	0.4538
	Toluene	0.560[b]	92.1	0.8622	9.358	97.6	0.4498
	Methanol	0.539	32.0	0.7864[g]	24.543	34.8	0.4854
	n-Octane	0.511	114.23	0.6986[g]	6.116	139.9	0.4849
	n-Heptane	0.390	100.20	0.6795[g]	6.781	123.7	0.4949
	Acetonitrile	0.347	41.1	0.7765[g]	18.915	45.8	0.4781
	Acetone	0.306[b]	58.1	0.7844[g]	13.506	62.2	0.4938
	n-Hexane	0.296	86.2	0.6548	7.598	107.5	0.5080
299.15	n-Hexane	0.293	86.2	0.6539[a]	7.588	107.5	0.5087
303.15	n-Octane	0.482	114.23	0.6947[a]	6.082	139.9	0.4878
	n-Heptane	0.371	100.20	0.6752[g]	6.739	123.7	0.4981
308.15	Benzene	0.524	78.1	0.8629[a]	11.047	81.1	0.4605
313.15	Ethanol	0.810	46.1	0.7731[a]	16.782	51.0	0.4847
	Methanol	0.447	32.0	0.7733[a]	24.134	34.8	0.4939
	n-Heptane	0.336	100.20	0.6665	6.652	123.7	0.5045
	n-Hexane	0.259	86.2	0.6409	7.437	107.5	0.5184
323.15	n-Heptane	0.306	100.20	0.6579	6.566	123.7	0.5109
333.15	2-Propanol	0.807[e]	60.1	0.7472[a]	12.434	67.2	0.4971
	Cyclohexane	0.534	84.2	0.7401	8.794	97.0	0.4862
	n-Heptane	0.281	100.20	0.6491	6.478	123.7	0.5175
	n-Hexane	0.219	86.2	0.6218	7.216	107.5	0.5328
343.15	n-Heptane	0.258	100.20	0.6402	6.389	123.7	0.5241
353.15	n-Heptane	0.237	100.20	0.6311	6.298	123.7	0.5309

[a]From Ref. 84 except where noted otherwise.
[b]From Ref. 48.
[c]From Ref. 86 except where noted otherwise.
[d]Average value from Refs. 39–42.
[e]Average value from Refs. 48 and 85.
[f]Average value from Refs. 48 and 84.
[g]From Ref. 87.

FSE relation. Recently, a MD simulation study by Whitman *et al.*[88] has found that for a solute of fixed molecular mass, the diffusive flux of that solute decreases as the molecular mass of solvent increases. This means that the diffusion rate of a solute is dependent on the mass of the solvent molecule, i.e., the greater the solvent mass is, the smaller the diffusivity of the solute would be. Interestingly, March[89] has also shown from previous theoretical study[90] of liquid metals that at the melting temperature T_m of liquid metal,

$$D_s^{-1} \propto M^{1/2}\rho^{1/3}/T_m^{1/2}, \qquad (13)$$

where D_s is the self-diffusion coefficient, M is the atomic mass, and ρ is the number density of the atoms. For tracer diffusion in this study, however, we have found that at any temperature there exists a similar relation with weaker mass dependence,

$$D_{12}^{-1} \propto M_2^{1/4}\rho_2^{1/3}, \qquad (14)$$

where M_2 is the molecular mass and ρ_2 is the molar density (number density in mol cm^{-3}) of the solvent, and that Eq. (14) is useful as a component for mending the inadequacy of the FSE relation. The generally weak mass dependence of diffusion has already been discussed by several authors.[19, 20] By combining Eqs. (11) and (14), a modified FSE relation can be written as

$$D_{12}^{-1} \propto \eta^t M_2^{1/4}\rho_2^{1/3}. \qquad (15)$$

The values of M_2 and ρ_2 for different solvents are given in Table IV. Following Eq. (12), we write for Eq. (15) as

$$\log\left(D_{12}^{-1}/M_2^{1/4}\rho_2^{1/3}\right) = z_2 + m\log\eta, \qquad (16)$$

where z_2 is a constant and m is used to distinguish itself from t. Although both t and m are slopes of the log–log plots, nonetheless their values should be different because of the additional component $M_2^{1/4}\rho_2^{1/3}$ in Eq. (16). When Eq. (16) is used to fit the 9 sets of data, linear lines with better regression results are obtained as compared to those using Eq. (12). The m values calculated for the 9 sets of data are displayed in Table III along with the t values for comparison. As expected, the m values are slightly different from those of t, with m being generally greater. This demonstrates that the t values in the FSE relation can indeed be affected by density and hence temperature and pressure. One aspect of the m values for the 9 sets of data is that they are even closer together than the t values in the present study. The m values range from 0.706 to 0.737, with an average of 0.723 ± 0.010. More importantly, by using Eq. (16) the average % deviation between the experimental and the calculated values of D_{12} are from 2.2% to 4.9% only. The maximum deviation for individual data is down to 10.1% (toluene in chlorobenzene), and the overall average deviation for the 9 sets of data is reduced from 6.9% to 3.6%. This result is a significant improvement over that of the FSE relation of Eq. (11).

Despite the improvement made by Eq. (16), however, a more careful examination of the results reveals that the experimental diffusivities in aromatic solvents are consistently and largely overestimated by the calculated values. We assumed at first that this was probably due to the particular chemical nature or structure of the aromatic solvent molecules. By closer inspection of the physical properties of the solvents in this study, we have found that the molecules are comparatively more compact in the aromatic solvents than in most other solvents. The free space available for molecules is relatively smaller in aromatic solvents. The ratio $\bar{V}_f/\bar{V}_m$ between the molar free volume $\bar{V}_f$ and the molar volume $\bar{V}_m$ of a solvent can be defined as

$$\bar{V}_f/\bar{V}_m = \frac{\bar{V}_m - N_A V_2}{\bar{V}_m}, \qquad (17)$$

where N_A is the Avogadro number and V_2 is the VDW volume of the solvent molecule. The ratio in Eq. (17) is a dimensionless fraction, and the values of this free volume fraction for various solvents at different temperatures are given in Table IV.

Free volume theory, which has affinity with the kinetic theory, has received considerable attention in the past few decades, and there are many reports on the successful use of that theory for the study of diffusion in the literature.[51,61,91–96] There are different approaches of using the free volume theory, and the simplest is probably the one given by Hildebrand.[91] Based on Batschinski's equation[97] for viscosity, Hiddebrand suggested for self diffusivity D_s the following:

$$D_s \propto \frac{\bar{V}_m - \bar{V}_o}{\bar{V}_o}, \qquad (18)$$

where $\bar{V}_o$ is the molar volume at which viscous flow ceases, i.e., a constant which should be closely related to the volume occupied by a mole of molecules as hard spheres.[21] Equation (18) and similar relations have been successfully applied by some investigators,[15,51,61,91] although Ertl and Dullien[92] have found that Eq. (18) is better expressed by raising the term $\left(\bar{V}_m - \bar{V}_o\right)/\bar{V}_o$ to a power greater than unity. In this work, we propose a slight modification of Eq. (18) that

$$D_{12} \propto \frac{\bar{V}_m - N_A V_2}{\bar{V}_m}. \qquad (19)$$

It follows from Eq. (17) that we can rewrite Eq. (19) as

$$D_{12} \propto \bar{V}_f/\bar{V}_m. \qquad (20)$$

This new free volume relation is physically reasonable as more free volume available would provide more voids or "holes" for molecules to jump into and hence promote diffusion. In addition, relatively more free volume may allow ease of relaxation of solvent molecules, which can probably enhance solute diffusion also.

By combining Eqs. (15) and (20), one can obtain the following relation:

$$D_{12}^{-1} \propto \eta^t M_2^{1/4}\rho_2^{1/3}/(\bar{V}_f/\bar{V}_m). \qquad (21)$$

The values of $\bar{V}_f/\bar{V}_m$ for different solvents are shown in Table IV. Similar to Eq. (16), we can express Eq. (21) as

$$\log\left[D_{12}^{-1}(\bar{V}_f/\bar{V}_m)/\left(M_2^{1/4}\rho_2^{1/3}\right)\right] = z_3 + y\log\eta, \qquad (22)$$

where z_3 and y (similar to t and m) are constants. When the 9 sets of data are fitted by using Eq. (22), very satisfactory regression results are yielded. The y values obtained are different from those of t and m as expected, and they are all given in Table III for comparison. The y values in the table clearly show that they are generally smaller than those of t and m. The values of y for the 9 sets of data also range narrowly from 0.647 to 0.686. Interestingly, the average value for y is 0.672 ± 0.011, a value which is very close to 2/3. By including the free volume fraction in Eq. (22), the average % deviation between the experimental and the calculated values of D_{12} for the 9 sets of data ranges from 1.5% to 3.1%, with the maximum deviation for individual data brought down to 6.0% (mesitylene in cyclohexane). The overall average deviation is significantly reduced to 2.1% only. The improvement made by modifying the FSE relation with different theories in the literature is indeed remarkable.

By using 2/3 as the mean value for y, Eq. (22) can be alternatively expressed as

$$D_{12}^{-1} = B\eta^{2/3}M_2^{1/4}\rho_2^{1/3}(\bar{V}_m/\bar{V}_f), \qquad (23)$$

where B is a constant. When D_{12}^{-1} is plotted against $\eta^{2/3}M_2^{1/4}\rho_2^{1/3}(\bar{V}_m/\bar{V}_f)$ for the 9 sets of data in Table III, straight lines with slope B are obtained, and all linear lines go through the origin zero. The plots are shown separately in Fig. 3 for easy reference, as some of the lines are very close together. It is noteworthy that the value of B generally increases as the size of solute increases. The values of B are
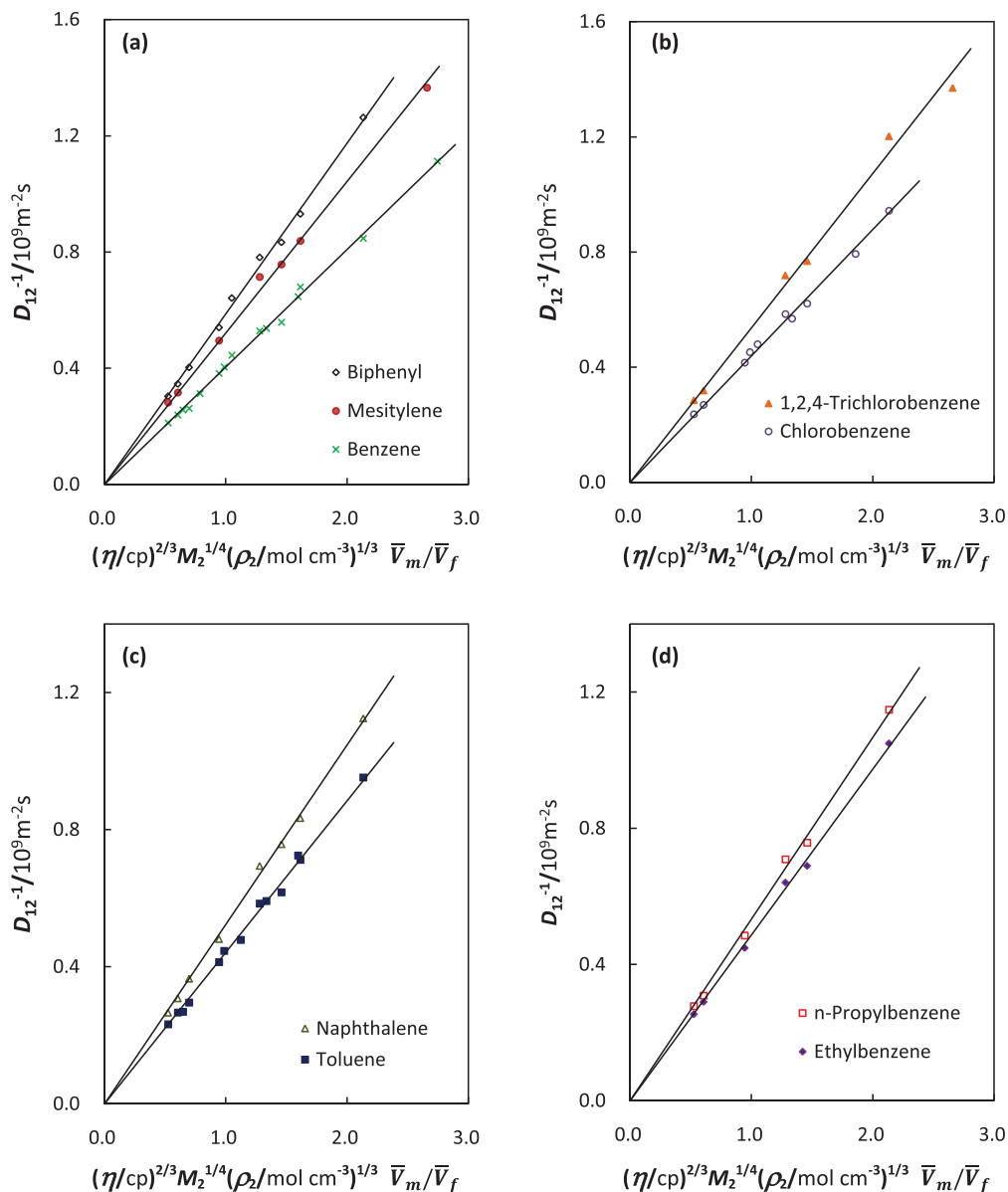
FIG. 3. Solvent dependence of $1/D_{12}$ for each of the aromatic solutes at 298.2 K.

also listed in Table III. It should be pointed out, however, that the calculated diffusivities using Eq. (22) with individual y values for the 9 sets of data are about the same as those using Eq. (23) with a fixed y value of 2/3. The overall average deviation between the experimental and the calculated diffusivities by using Eq. (23) is 2.3% as compared to 2.1% using Eq. (22). The difference is 0.2% only.

To summarize the study on the solvent dependence in this section, we first found that the FSE relation is inadequate after analyzing 80 data collected from different sources. By adding the contribution of free volume fraction as well as the mass and molar density of solvent, we have discovered that Eq. (23) is a much better representation of the solvent dependence for tracer diffusivities of pseudoplanar aromatic solutes. The development of Eq. (23) is based on relevant theories, computer studies, and experimental results. The solvents in this work include those of different molecular masses, shapes, and sizes as well as different properties such as viscosity, density, and

intermolecular bonding. Two interesting points emerge from the solute and solvent dependences found in this investigation. First, while the mass of solute is unimportant in tracer diffusion, the diffusivity is nonetheless weakly dependent on the mass of the solvent molecule. The second feature is that as the solute size (as well as shape) is significant in determining the tracer diffusivities, the effect of size and shape of solvent molecules is nonetheless not obvious in the solvent dependence. According to the VDW picture for nonassociated molecules in liquids,[11] motions of molecules should depend largely on the size and shape of the molecules (i.e., the short range repulsive intermolecular forces). One possible explanation is that the effects of solvent shape and size are probably already incorporated in the viscosity and the free volume fraction terms, i.e., viscosity and free volume fraction are shape and size related. For example, pseudoplanar solvents are generally of relatively lower value in free volume fraction as compared with other solvents. Another example is

that for molecules of the same chemical class the larger the solvent molecule is, the higher its viscosity would be. These relations can be seen from the solvent properties in Table IV. It should also be noted that depending on the size of the solute molecule, the values of the constant B in Eq. (23) are different (see Table III). Whether viscosity's exponent y value in Eq. (23) would vary with the shape of solutes is not known in this work; however, the present investigation indicates that changes in y with respect to solute size is quite small for the range of solutes studied.

C. Idealized relation and temperature dependence

The SE relation of Eq. (1) was originally derived from the well-known Einstein equation:

$$D_{12} = \frac{k_B T}{\xi}, \qquad (24)$$

where ξ is the frictional coefficient related to the retarding force acting on a solute by solvent in the diffusion process. For mutual diffusion, ξ is expected to be solute and solvent dependent. If the solute can be considered as a spherical and very large particle diffusing in a continuum of solvent medium, the Stokes law is applicable, i.e.,

$$\xi = 6\pi r_1 \eta. \qquad (25)$$

The SE relation was thus established by combining Eqs. (24) and (25). In real liquid systems, however, many solutes (except macromolecules) are neither spherical in shape nor very large in size as compared to solvent molecules. In such real systems, the SE relation is often invalid. The question is what expression ξ should be for diffusion of normal molecules in liquids when the SE relation is inapplicable.

The Stokes law can be viewed as a combination of two functions, one of solute's radius r_1 and the other of solvent's viscosity η. This relation in connection with friction between solute and solvent leads us to postulate that ξ for normal sized solute and solvent molecules is also a product of two functions, i.e.,

$$\xi = f(u) g(v), \qquad (26)$$

where $f(u)$ is dependent on solute and $g(v)$ on solvent. Equation (26) is an idealized equation of which we have no proof, except by testing it against diffusion data. While the Stokes law of Eq. (25) is ideal for large spherical solutes, the focus of the present study is on nonassociated pseudoplanar solutes with size not huge as compared to solvent molecules. By substituting Eq. (26) into Eq. (24), we can write

$$D_{12} = \frac{k_B T}{f(u) g(v)}. \qquad (27)$$

From the result of the solute dependence of Eq. (4), $f(u)$ can be given by

$$f(u) \propto V_1 + b_1, \qquad (28)$$

where b_1 is a constant. Similarly from Eq. (23) for the solvent dependence, we can have

$$g(v) \propto \eta^{2/3} M_2^{1/4} \rho^{1/3} (\bar{V}_m / \bar{V}_f). \qquad (29)$$

Combining Eqs. (27)–(29), one can get the following relation:

$$D_{12} \propto \frac{k_B T}{(V_1 + b_1)(\eta^{2/3} M_2^{1/4} \rho_2^{1/3} \bar{V}_m / \bar{V}_f)}. \qquad (30)$$

This idealized relation, if correct, should be valid only for solutes of pseudoplanar shape. One of the reasons is because the viscosity's exponent may be different from 2/3 for other shapes of solute molecules. Equation (30) can be alternatively expressed as

$$D_{12} = \frac{T}{(pV_1 + q)(\eta^{2/3} M_2^{1/4} \rho_2^{1/3} \bar{V}_m / \bar{V}_f)}, \qquad (31)$$

where p and q are constants. Hence, at constant T, when D_{12}^{-1} is plotted against $(\eta^{2/3} M_2^{1/4} \rho_2^{1/3} \bar{V}_m / \bar{V}_f)$ for a given solute as in Fig. 3, the slope should be $(pV_1 + q)T^{-1}$. Similarly, when D_{12}^{-1} is plotted against V_1 at constant T for a given solvent (as in Figs. 1 and 2), the quantity $p(\eta^{2/3} M_2^{1/4} \rho_2^{1/3} \bar{V}_m / \bar{V}_f)T^{-1}$ would be the slope. At a constant temperature (e.g., 298.2 K), the requirement of all the slopes of straight lines is that p and q are universal constants for all solutes as well as solvents. From Eq. (31), it can be easily seen at constant T that as V_1 increases, the slope for the solvent dependence also increases. This is consistent with the B values in Eq. (23) for different solutes as we have pointed out in Sec. III B.

We have attempted to use Eq. (31) to fit the data (without units) at 298.2 K in Tables III and IV. All 80 diffusion data are well fitted by the equation. With $p = 0.783 \pm 0.021$ and $q = 56.0 \pm 2.4$, Eq. (31) fits all data to within an average absolute error of $\pm 2.4\%$, the standard deviation being only $\pm 1.7\%$. This excellent agreement between the experimental and calculated diffusivities supports that our assumption of Eq. (26) and hence Eq. (27) is correct for the tracer diffusion of nonassociated pseudoplanar solutes.

Table V shows the tracer diffusivities at various temperatures, which have been collected from different studies in the literature. The data were measured by different investigators using different techniques. Only diffusivities measured below the normal boiling point of solvent under 1 atm were used. These data, together with those at 298.2 K in Table III as well as the solvent data in Table IV, have been employed (in dimensionless form again) to test the temperature dependence of Eq. (31). It is found that the equation fits all 176 data almost equally well with $p = 0.800 \pm 0.008$ and $q = 53.9 \pm 1.1$. The % average error is $\pm 2.8\%$, and the standard deviation of the % errors is $\pm 2.1\%$. The maximum error is 8.9%. The calculated values from Eq. (31) are shown in Tables III and V along with the experimental diffusivities for comparison. It should be noted that the diffusion data, ranging from 0.538 to 7.03×10^{-9} m^2 s^{-1}, cover temperatures from 273.2 K to 353.2 K, V_1 from 81.1 Å^3 to 509.1 Å^3, η from 0.219 cp to 3.063 cp, and M_2 from 32.04 to 226.4. It is of particular interest to note that large solutes such as rubrene (V_1 = 509.1 Å^3) and pyrene (V_1 = 187.0 Å^3) are well described by the equation. Although only nonassociated aromatic solutes were studied in this work, the solvents involved actually included polar, nonpolar, and hydrogen-boned molecules of different shapes and sizes. In consideration of the

TABLE V. Experimental and calculated tracer diffusivities at different temperatures.

Temp.(K)[a]	Solvent	Solute[b,c]	D_{12} (10^{-9} m^2 s^{-1})[d]	Refs.	Calc. D_{12} (10^{-9}m^{2}s^{-1})[e]
273.15	n-Hexane	Anthracene	2.33 ± 0.06	14	2.23
		Benzene	3.40 ± 0.09	14	3.56
		Mesitylene	2.57 ± 0.06	14	2.67
		Naphthalene	2.66 ± 0.07	14	2.74
		Toluene	3.21 ± 0.08	14	3.21
		p-Xylene	2.95 ± 0.07	14	2.91
280.05	n-Heptane	Toluene	2.95 ± 0.06	81	2.77
298.15[a]	Acetone	p-Chlorotoluene	3.50 ± 0.03	29	3.41
		m-Dichlorobenzene	3.38 ± 0.04	29	3.42
		o-Dichlorobenzene	3.35 ± 0.03	29	3.42
		p-Dichlorobenzene	3.46 ± 0.04	29	3.42
		m-Xylene	3.42 ± 0.03	29	3.40
		o-Xylene	3.39 ± 0.04	29	3.40
		p-Xylene	3.52 ± 0.04	29	3.40
	Acetonitrile	Bromobezene	3.14 ± 0.03	46	3.15
	Carbon tetrachloride	Anthracene	1.026	80	0.974
		Hexachlorobenzene	0.922	80	0.943
		Phenanthrene	1.03 ± 0.01	50	0.974
	Chlorobenzene	Bromobezene	1.66 ± 0.02	78	1.64
	Cyclohexane	Hexamethylbenzene	1.09 ± 0.01	This work	1.18
		Phenanthrene	1.199 ± 0002	51	1.23
		p-xylene	1.645 ± 0.002	51	1.61
	Ethanol	p-Chlorotoluene	1.54 ± 0.02	29	1.41
		m-Dichlorobenzene	1.43 ± 0.01	29	1.42
		o-Dichlorobenzene	1.37 ± 0.01	29	1.42
		p-Dichlorobenzene	1.54 ± 0.02	29	1.42
		m-Xylene	1.44 ± 0.02	29	1.41
		o-Xylene	1.40 ± 0.01	29	1.41
		p-Xylene	1.54 ± 0.02	29	1.41
	n-Hexadecane	Anthracene	0.538	49	0.574
	n-Hexane	Anthracene	3.09	49	3.00
		Bromobezene	3.86 ± 0.04	46	4.18
		Phenanthrene	3.08 ± 0.03	50	3.00
		Pyrene	2.86	49	2.80
		1,2,4-Trimethylbenzene	3.57 ± 0.03	This work	3.59
	Methanol	1-Methylnaphthalene	1.90 ± 0.02	35	1.89
	n-Octane	Anthracene	2.03	49	2.00
	n-Tetradecane	p-Chlorotoluene	1.01 ± 0.01	29	0.965
		m-Dichlorobenzene	0.936 ± 0.006	29	0.968
		o-Dichlorobenzene	0.888 ± 0.006	29	0.968
		p-Dichlorobenzene	1.00 ± 0.01	29	0.968
		m-Xylene	0.943 ± 0.005	29	0.963
		o-Xylene	0.892 ± 0.007	29	0.963
		p-Xylene	1.02 ± 0.01	29	0.963
	Toluene	Bromobezene	2.05 ± 0.02	46	2.22
299.15	n-Hexane	Anthracene	3.13 ± 0.08	14	3.04
		Benzene	4.66 ± 0.12	14	4.85
		Mesitylene	3.45 ± 0.09	14	3.64
		Naphthalene	3.65 ± 0.09	14	3.74
		Toluene	4.38 ± 0.11	14	4.37
		p-Xylene	4.07 ± 0.10	14	3.97
303.15	n-Heptane	Anthracene	2.68	49	2.58
		Biphenyl	2.77	49	2.78
	n-Octane	Anthracene	2.16	49	2.13
		Biphenyl	2.30	49	2.29

TABLE V. (*Continued.*)

Temp.(K)[a]	Solvent	Solute[b,c]	D_{12} (10^{-9} m^2 s^{-1})[d]	Refs.	Calc. D_{12} (10^{-9} m^{2}s^{-1})[e]
308.15	Benzene	Biphenyl	1.847	83	1.88
313.15	Ethanol	Benzene	2.28 ± 0.02	53	2.21
		Mesitylene	1.69 ± 0.02	53	1.65
		Naphthalene	1.73 ± 0.02	53	1.70
		Phenanthrene	1.43 ± 0.01	53	1.38
		Toluene	2.12 ± 0.02	53	1.99
	Methanol	Benzene	3.26 ± 0.07	98	3.24
		Mesitylene	2.51 ± 0.05	98	2.43
		Naphthalene	2.61 ± 0.05	98	2.50
		Phenanthrene	2.21 ± 0.04	98	2.03
		Toluene	3.05 ± 0.06	98	2.92
	n-Heptane	Benzene	4.47	38	4.63
		Toluene	4.33 ± 0.09	81	4.16
	n-Hexane	Anthracene	3.71 ± 0.09	14	3.54
		Benzene	5.47 ± 0.13	14	5.66
		Mesitylene	4.16 ± 0.10	14	4.24
		Naphthalene	4.24 ± 0.11	14	4.36
		Rubrene	1.46 ± 0.04	14	1.46
		Toluene	5.00 ± 0.12	14	5.09
		p-Xylene	4.61 ± 0.11	14	4.63
323.15	*n*-Heptane	Benzene	5.06	38	5.17
333.15	Cyclohexane	Benzene	3.18 ± 0.02	51	3.32
		Mesitylene	2.40 ± 0.01	51	2.48
		Naphthalene	2.51 ± 0.02	51	2.55
		Phenanthrene	2.120 ± 0.004	51	2.08
		Toluene	2.968 ± 0.006	51	2.98
		p-Xylene	2.85 ± 0.03	51	2.71
	n-Heptane	Benzene	5.64	38	5.74
	n-Hexane	Benzene	6.92	14, 54	6.99
		Mesitylene	5.13	14, 54	5.24
		Naphthalene	5.42	14, 54	5.38
		Phenanthrene	4.49 ± 0.04	54	4.38
		Rubrene	1.76 ± 0.04	14	1.80
		Toluene	6.25	14, 54	6.29
		p-Xylene	5.77 ± 0.07	54	5.72
	2-Propanol	Benzene	2.39 ± 0.05	98	2.50
		Naphthalene	1.80 ± 0.04	98	1.92
		Phenanthrene	1.47 ± 0.03	98	1.56
		Toluene	2.21 ± 0.04	98	2.25
343.15	*n*-Heptane	Benzene	6.33	38	6.37
353.15	*n*-Heptane	Benzene	7.03	38	7.06

[a]Data at 298.15 K are those not listed in Table III.
[b]Values of V_1 for the isomers of xylene, chlorotoluene, and dichlorobenzene are 114.2 Å^3, 113.7 Å^3, and 113.2 Å^3, respectively.
[c]V_1 Values for 1-methylnaphthalene, hexachlorobenzene, and rubrene are 141.9 Å^3, 177.6 Å^3, and 509.1 Å^3, respectively; values for other solutes are given in Table I.
[d]Value is average where two or more data are available in a given reference or different references.
[e]Calculated from Eq. (31) with $p = 0.800$ and $q = 53.9$.

experimental errors in different measurements of the diffusivities, the slight differences in the shape of the pseudoplanar solutes as well as the small uncertainties in the data of the solvent and solute properties, the prediction of a total of 176 data at different temperatures by Eq. (31) within an average deviation of ±2.8% clearly indicates the success of the equation. Also, there are only two parameters p and q in the relation that are needed for describing all the data. It should be pointed out that only temperature independent VDW volumes of solutes and solvent molecules are constantly used throughout this study. More importantly, Eq. (31) can account well for a wide range of tracer diffusivities of normal sized molecules that cannot be handled by the SE relation. This equation pieces the relevant theoretical and computing results

as well as experimental facts of general significance together to yield a synergistic effect for describing a large number of diffusion data, while each of the components has its own merits in other studies of smaller systems.

IV. CONCLUSION

For diffusion of solutes with sizes comparable to solvent molecules, the SE relation is generally known to be inapplicable. In this work, we present new tracer diffusivities of nonassociated aromatic solutes in *n*-hexane and cyclohexane at 298.2 K. These data, combined with other diffusion coefficients in the literature, are utilized to find out separately the solute and solvent dependences of tracer diffusivities in molecular liquids. Based on these dependences, a model is developed for describing the diffusion behavior of nonassociated pseudoplanar solutes of sizes which cannot be treated by the SE relation.

The solute dependence found in this study is quite straightforward. For pseudoplanar solutes diffusing in a given solvent at constant temperature, there exists a linear relationship between the reciprocal of the tracer diffusivities ($1/D_{12}$) and the VDW volume of the solutes. This linear relationship is shown by all 13 sets of data obtained in this work as well as from different sources in the literature. For solvent dependence, the present work finds that the FSE relation is inadequate. Our study of 80 data shows that Eq. (23), which also includes the molar density, the molecular mass, and the reciprocal of the free volume fraction of solvent, is a better representation of the solvent dependence. An interesting feature of the result is that while solute mass is insignificant in the solute dependence, tracer diffusivity is weakly dependent on the mass of the solvent molecule. Another worthy remark is that as the size of the pseudoplanar solutes is important in the solute dependence, it appears that the effects of size and shape of solvent molecules are not apparent in the expression of the solvent dependence.

The present study contributes a relation built upon the framework of the Einstein equation to account for the tracer diffusivities of nonassociated aromatic solutes in liquids. The newly developed relation, which includes temperature dependence of diffusivities, can be considered as a modification of the SE relation by replacing the Stokes law with the product of the solute and solvent dependences found in this work. Based on different theoretical and computing results as well as experimental evidences, this semi-empirical relation, Eq. (31), is capable of correlating 176 diffusion data ranging from 0.538 to 7.03×10^{-9} m^2 s^{-1} to within an average error of ±2.8%. The data cover solutes of different sizes from 81.1 Å^3 to 509.1 Å^3, solvents of different viscosities from 0.219 cp to 3.063 cp, and temperatures from 273.2 K to 353.2 K. Solvent molecules are also different in size, shape, and chemical nature. While each of the existing theories of diffusion in the literature, e.g., the hydrodynamic theory and the kinetic theory, has its own merits in describing the diffusion behavior of molecules in liquids, it appears that none of them alone could predict the diffusivities of a wide range of normal sized molecules well. The success of Eq. (31) suggests that an approach by combining the useful parts of some existing theories, together with

the experimental facts of general significance, may result in complementary or synergistic effects. Although the relation is idealized for pseudoplanar solutes, it can probably be modified and extended to describe the diffusion data of other types of solutes. A study of a similar relation for pseudospherical as well as other solutes is being undertaken in this laboratory.

[1] D. F. Evans, C. Chan, and B. C. Lamartine, J. Am. Chem. Soc. **99**, 6492 (1977).
[2] D. F. Evans, T. Tominaga, and H. T. Davis, J. Chem. Phys. **74**, 1298 (1981).
[3] D. F. Evans, T. Tominaga, and C. Chan, J. Solution Chem. **8**, 461 (1979).
[4] S. K. Kumar, G. Szamel, and J. F. Douglas, J. Chem. Phys. **124**, 214501 (2006).
[5] R. Walser, A. E. Mark, and W. F. van Gunsteren, Chem. Phys. Lett. **303**, 583 (1999).
[6] F. Ould-Kaddour and J.-L. Barrat, Phys. Rev. A **45**, 2308 (1992).
[7] S. Bhattacharyya and B. Bagchi, J. Chem. Phys. **106**, 1757 (1997).
[8] E. L. Cussler, *Diffusion, Mass Transfer in Fluid Systems*, 2nd ed. (Cambridge University Press, Cambridge, England, 1997).
[9] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
[10] D. Chandler, J. Chem. Phys. **60**, 3500–3508 (1974).
[11] D. Chandler, J. D. Weeks, and H. C. Andersen, Science **220**, 787 (1983).
[12] S. J. Bertucci and W. H. Flygare, J. Chem. Phys. **63**, 1 (1975).
[13] K. J. Czworniak, H. C. Andersen, and R. Pecora, Chem. Phys. **11**, 451 (1975).
[14] J. H. Dymond, J. Phys. Chem. **85**, 3291 (1981).
[15] M. A. Matthews and A. Akgerman, J. Chem. Phys. **87**, 2285 (1987).
[16] A. Greiner-Schmid, S. Wappmann, M. Has, and H.-D. Lüdemann, J. Chem. Phys. **94**, 5643 (1991).
[17] J. Jonas, D. Hasha, and S. G. Huang, J. Chem. Phys. **71**, 3996 (1979).
[18] A. J. Esteal and L. A. Woolf, Physica B **124**, 182 (1984).
[19] B. Bagchi and S. Bhattacharyya, Adv. Chem. Phys. **116**, 67 (2001).
[20] S. M. Ali, A. Samanta, and S. K. Ghosh, J. Chem. Phys. **114**, 10419 (2001); Chem. Phys. Lett. **357**, 217 (2002).
[21] H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids* (Butterworths, London, 1984).
[22] See, for example, (a) O. Kravchenko and M. Thachuk, J. Chem. Phys. **136**, 044520 (2012); **134**, 114310 (2011); (b) Y. Lü, H. Cheng, and M. Chen, *ibid.* **136**, 214505 (2012); (c) G. Guevara-Carrion, J. Vrabec, and H. Hasse, *ibid.* **134**, 074508 (2011); (d) A. E. Nasrabad, *ibid.* **129**, 244508 (2008); (e) R. O. Sokolovskii, M. Thachuk, and G. N. Patey, *ibid.* **125**, 204502 (2006); (f) R. K. Murarka, S. Bhattacharyya, and B. Bagchi, *ibid.* **117**, 10730 (2002); (g) K. Meier, A. Laesecke, and S. Kabelac, *ibid.* **121**, 9526 (2004); (h) R. Visanthi, S. Bhattacharyya, and B. Bagchi, *ibid.* **116**, 1092 (2002).
[23] S. A. Egorov, J. Chem. Phys. **128**, 144508 (2008).
[24] T. Yamaguchi and S. Koda, J. Chem. Phys. **134**, 234506 (2011).
[25] (a) G. Srinivas, S. Bhattacharyya, and B. Bagchi, J. Chem. Phys. **110**, 4477 (1999); (b) S. Bhattacharyya and B. Bagchi, Phys. Rev. E **61**, 3850 (2000).
[26] T. Yamaguchi, N. Matubayasi, and M. Nakahara, J. Chem. Phys. **115**, 422 (2001).
[27] See, for example, Y. Qin and B. C. Eu, J. Phys. Chem. B **113**, 4751 (2009); Y.-L. S. Tse and H. C. Andersen, J. Chem. Phys. **136**, 024904 (2012); D. Matuszak, G. L. Aranovich, and M. D. Donohue, *ibid.* **121**, 426 (2004); A. E. Nasrabad, *ibid.* **130**, 024503 (2009); P. Nigra and G. T. Evans, *ibid.* **122**, 244508 (2005); E. H. Feng and H. C. Andersen, *ibid.* **121**, 3598 (2004); B. C. Eu, J. Phys. Chem. A **110**, 831 (2006).
[28] T. C. Chan, J. Chem. Phys. **79**, 3591 (1983).
[29] T. C. Chan, J. Chem. Phys. **80**, 5862 (1984).
[30] T. C. Chan and M. L. Chan, J. Chem. Soc., Faraday Trans. **88**, 2371 (1992); **89**, 867 (1993).

[31] M. L. Chan and T. C. Chan, J. Phys. Chem. **99**, 5765 (1995).

[32] N. Chen and T. C. Chan, Chem. Commun. **1997**, 719.

[33] T. C. Chan, N. L. Ma, and N. Chen, J. Chem. Phys. **107**, 1890 (1997).

[34] T. C. Chan, N. Chen, and J. G. Lu, J. Phys. Chem. A **102**, 9087 (1998).

[35] J. G. Lu, R. Kong, and T. C. Chan, J. Chem. Phys. **110**, 3003 (1999).

[36] S. Chen, J. Xu, and T. C. Chan, Chem. Commun. **2002**, 898.

[37] G. I. Taylor, Proc. R. Soc. London, Ser. A **219**, 186 (1953); **225**, 473 (1954).

[38] E. Grushka and E. J. Kikta, Jr., J. Am. Chem. Soc. **98**, 643 (1976).

[39] J. T. Edward, Chem. Ind., London **1956**, 774.

[40] A. Bondi, J. Phys. Chem. **68**, 441 (1964).

[41] A. E. Luzkii, Russ. J. Phys. Chem. **28**, 204 (1954).

[42] A. I. Kitaigorodskii, *Organic Chemical Crystallography* (Consultants Bureau, New York, 1961).

[43] K. R. Harris, C. K. N. Pua, and P. J. Dunlop, J. Phys. Chem. **74**, 3518 (1970).

[44] J. G. Albright and K. Aoyagi, J. Chem. Phys. **64**, 81 (1976).

[45] J. Leffler and H. T. Cullinan, Jr., Ind. Eng. Chem. Fundam. **9**, 88 (1970).

[46] A. J. Easteal and L. A. Woolf, J. Chem. Soc., Faraday Trans. 1 **80**, 1287 (1984).

[47] J. H. Dymond and L. A. Woolf, J. Chem. Soc., Faraday Trans. 1 **78**, 991 (1982).

[48] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide, 88th ed. (CRC Press, Boca Raton, Florida, 2008).

[49] B. A. Kowert, N. C. Dang, K. T. Sobush, and L. G. Seele III, J. Phys. Chem. A **105**, 1232 (2001).

[50] D. L. Bidlack, T. K. Kett, C. M. Kelly, and D. K. Anderson, J. Chem. Eng. Data **14**, 342 (1969).

[51] C. K. J. Sun and S. H. Chen, AIChE J. **31**, 1510 (1985).

[52] R. Mills, J. Phys. Chem. **69**, 3116 (1965); L. Rodwin, J. A. Harpst, and P. A. Lyons, *ibid.* **69**, 2783 (1965).

[53] C. K. J. Sun and S. H. Chen, AIChE J. **32**, 1367 (1986).

[54] C. K. J. Sun and S. H. Chen, Chem. Eng. Sci. **40**, 2217 (1985).

[55] R. Zwanzig and A. K. Harrison, J. Chem. Phys. **83**, 5861 (1985).

[56] S. H. Chen, H. T. Davis, and D. F. Evans, J. Chem. Phys. **75**, 1422 (1981).

[57] W. Hayduk and S. C. Cheng, Chem. Eng. Sci. **26**, 635 (1971).

[58] T. G. Hiss and E. L. Cussler, AIChE J. **19**, 698 (1973).

[59] T. Funazukuri, C. Y. Kong, and S. Kagei, J. Supercrit. Fluids **46**, 280 (2008); C. Wakai and M. Nakahara, J. Chem. Phys. **100**, 8347 (1994).

[60] G. L. Pollack, Phys. Rev. A **23**, 2660 (1981).

[61] S. H. Chen, H. T. Davis, and D. F. Evans, J. Chem. Phys. **77**, 2540 (1982).

[62] S. H. Chen, D. F. Evans, and H. T. Davis, AIChE J. **29**, 640 (1983).

[63] G. L. Pollack and J. J. Enyeart, Phys. Rev. A **31**, 980 (1985).

[64] G. L. Pollack, R. P. Kennan, J. F. Himm, and D. R. Stump, J. Chem. Phys. **92**, 625 (1990).

[65] B. A. Kowert and N. C. Dang, J. Phys. Chem. A **103**, 779 (1999).

[66] B. A. Kowert, N. C. Dang, J. P. Reed, K. T. Sobush, and L. G. Seele III, J. Phys. Chem. A **104**, 8823 (2000).

[67] S. Bhattacharyya and B. Bagchi, J. Chem. Phys. **107**, 5852 (1997).

[68] K. R. Harris, J. Chem. Phys. **131**, 054503 (2009).

[69] K. R. Harris, J. Chem. Phys. **132**, 231103 (2010).

[70] B. A. Kowert, K. T. Sobush, N. C. Dang, L. G. Seele III, C. F. Fuqua, and C. L. Mapes, Chem. Phys. Lett. **353**, 95 (2002).

[71] B. A. Kowert, K. T. Sobush, C. F. Fuqua, C. L. Mapes, J. B. Jones, and J. A. Zahm, J. Phys. Chem. A **107**, 4790 (2003).

[72] A. S. Chauhan, R. Ravi, and R. P. Chhabra, Chem. Phys. **252**, 227 (2000).

[73] D. M. Heyes and A. C. Branka, Phys. Chem. Chem. Phys. **7**, 1220 (2005).

[74] J. R. Rajian, W. Huang, R. Richert, and E. L. Ouitevis, J. Chem. Phys. **124**, 014510 (2006).

[75] J. R. Rajian and E. L. Ouitevis, J. Chem. Phys. **126**, 224506 (2007).

[76] B. A. Kowert, R. M. Turner II, and C. V. C. Caldwell, Chem. Phys. **344**, 114 (2008).

[77] R. Mills, J. Phys. Chem. **67**, 600 (1963).

[78] C. S. Caldwell and A. L. Babb, J. Phys. Chem. **60**, 51 (1956).

[79] I. R. Shankland, P. J. Dunlop, and L. W. Barr, Phys. Rev. B **12**, 2249 (1975).

[80] L. G. Longsworth, J. Colloid Interface Sci. **22**, 3 (1966).

[81] P. Chang and C. R. Wilke, J. Phys. Chem. **59**, 592 (1955).

[82] T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, J. Am. Chem. Soc. **87**, 121 (1965).

[83] C. L. Sandquist and P. A. Lyons, J. Am. Chem. Soc. **76**, 4641 (1954).

[84] C. L. Yaws, *Chemical Properties Handbook* (McGraw-Hill, New York, 1999).

[85] D. S. Viswanath and G. Natarajan, *Data Book on the Viscosity of Liquids* (Hemisphere, New York, 1989).

[86] N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed. (Hemisphere, Washington, D.C., 1975).

[87] J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents*, 4th ed. (Wiley, New York, 1986).

[88] J. R. Whitman, G. L. Aranovich, and M. D. Donohue, J. Chem. Phys. **134**, 094303 (2011).

[89] N. H. March, J. Chem. Phys. **80**, 5345 (1984).

[90] R. C. Brown and N. H. March, Phys. Chem. Liq. **1**, 141 (1968).

[91] J. H. Hildebrand, Science **174**, 490 (1971).

[92] H. Ertl and F. A. L. Dullien, J. Phys. Chem. **77**, 3007 (1973).

[93] K. Rah and B. C. Eu, J. Chem. Phys. **115**, 2634 (2001); Phys. Rev. Lett. **88**, 065901 (2002).

[94] A. E. Nasrabad, N. M. Oghaz, and B. Haghighi, J. Chem. Phys. **129**, 024507 (2008).

[95] R. Laghaei, A. E. Nasrabad, and B. C. Eu, J. Phys. Chem. B **109**, 5873 (2005).

[96] A. E. Nasrabad, R. Laghaei, and B. C. Eu, J. Phys. Chem. B **109**, 8171 (2005).

[97] A. J. Batschinski, Z. Phys. Chem. **84**, 643 (1913).

[98] C. K. J. Sun and S. H. Chen, Ind. Eng. Chem. Res. **26**, 815 (1987).