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Relation of Tracer Diffusion Coefficient and Solvent Self-Diffusion Coefficient

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It is shown that the tracer diffusion and self-diffusion coefficients of liquids are in a simple linear relation with a constant coefficient, which depends on only the molecular size ratio and the mass ratio of the solute and the solvent molecule. With experimentally determined tracer diffusion and self-diffusion coefficients, the relation can be used for estimating the molecular sizes of polyatomic molecules. By estimation of the size ratio with the van der Waals radii of the constituent molecules, the relation is shown to account excellently for the experimental data on diffusion of various solutes, such as a series of benzene derivatives, ketones, alcohols, and so on, in organic solvents or water. The systems investigated include those in which the hydrogen bonding effects are expected to affect the diffusion of tracer molecules (e.g., alcohols in water and vice versa). The relation of diffusion coefficients presented is thus shown to be an excellent means to estimate molecular sizes from the data on diffusion coefficients measurable by various methods including NMR techniques.

I. Introduction

Molecular structures and sizes are important information in chemistry and physics that are indispensable in understanding physical and chemical properties of matter. As a matter of fact, the major portion of physical chemistry is devoted to developing methods to elucidate and estimate them. Transport properties of fluids provide an important class of methods to measure the aforementioned quantities among other physical properties of molecules. Notwithstanding their importance in studying physical and molecular properties of matter, they are difficult to calculate in good accuracy, particularly in the liquid density regime. Neither are all transport coefficients amenable to measurement at comparable precision and facility. Therefore the kind of difficulty mentioned can be much alleviated when there is a relation between transport coefficients, especially if one transport coefficient is more readily available than the other, either experimentally or theoretically. A celebrated example is the Stokes−Einstein (SE) relation,[1] which holds between the shear viscosity η of a solvent of molecular radius r_1, which is treated as a continuous medium, and the tracer diffusion coefficient of the solute with molecular radius r_2, which is assumed to be much larger than r_1; to be precise, r_2 should be of a macroscopic size. When this condition is not satisfied, the SE relation is considered inapplicable, but it is sometimes found still useful if a suitable adjustment is made to the value of r_2 and the boundary condition is modified. Such adjustments are empirical and there is no molecular theory foundation. In recent papers[2] on nonequilibrium statistical mechanics of liquids, relations similar to the SE relation have been shown to hold not only for the shear viscosity but also for other transport coefficients, such as the bulk viscosity and the thermal conductivity, of single component liquids. However, the coefficient factor depends on the intermolecular force and the equilibrium pair correlation function of the fluid unlike the one in the SE relation. They excellently account[2] for the density and temperature dependence of the transport coefficients mentioned.

The SE relation has seen frequent applications as a way to determine the size of the tracer (solute) molecule, but as mentioned earlier, it often requires an empirical correction factor in order for the experimental results to be properly accounted for, in particular, when $r_2 \lesssim r_1$. In this paper we propose a new, simple yet reliable relation that furnishes the size ratio of the solute and solvent molecules and thus enables us to estimate rather effectively the molecular sizes of the molecules involved. This method of estimating molecular sizes should be of considerable interest to physical organic chemistry and biochemistry.

Recently, Rah and Eu[3] have developed a theory of diffusion coefficients D_{12} of binary simple liquid mixtures

$$D_{12} = D_{12}^0 \exp(-v_{12}^0/v_f) \tag{1}$$

where D_{12}^0 is the Chapman−Enskog gas kinetic diffusion coefficient,[4] v_{12}^0 is the mean molecular volume of the mixture, and v_f is the free volume of the liquid, which can be calculated by means of statistical mechanics with the help of the generic van der Waals equation of state.[5] The formula (1) reduces to the corresponding self-diffusion coefficient[6] in the single component limit, e.g., for species 1

$$D_1 = D_1^0 \exp(-v_1^0/v_f) \tag{2}$$

where v_1^0 is related to v_{12}^0 by the relation $v_{12}^0 = v_1^0 X_1 + v_2^0 X_2$ with X_i ($i = 1, 2$) denoting the mole fraction of species i. The v_i^0 is the characteristic excluded volume proportional to the molecular volume of species i. A test of these free-volume theory formulas for D_{12} and D_1 shows that the Chapman−Enskog D_{12}^0 and D_1^0 can be respectively approximated, to a

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good accuracy, by the Chapman−Enskog formulas for the hard sphere fluid:

$$D_{12}^0 = \frac{3}{8\rho\sigma_{12}^2}\sqrt{\frac{k_BT}{2\mu}}$$

$$D_1^0 = \frac{3}{8\rho\sigma_1^2}\sqrt{\frac{k_BT}{m_1}} \tag{3}$$

where k_B is the Boltzmann constant, ρ is the number density, T is the absolute temperature, μ is the reduced mass of molecules 1 and 2, m_i ($i = 1, 2$) is the mass of species i, $\sigma_{12} = {}^1/_2(\sigma_1 + \sigma_2)$, and σ_i is the size parameter (an effective diameter) of the molecule of species i in the potential energy model employed to represent the intermolecular interactions. We develop a relation between the tracer diffusion coefficient D_t and the self-diffusion coefficient D_1 of liquid medium 1 and then test the relation against the experimental data available in the literature and the NMR pulse sequence data obtained by Kwak and Lafleur by using the van der Waals radii of the molecules calculated by means of the Edward method.[7] The agreement between theory and experiment is found excellent.

II. Relation between the Tracer and Self-Diffusion Coefficients

The diffusion coefficient D_{12} and the self-diffusion coefficient D_1 of the medium together with the Chapman−Enskog formulas for D_{12}^0 and D_1^0 given in eq 3 evidently give a relation with the proportionality coefficient depending on material parameters. The tracer diffusion coefficient D_t is the limiting density form of D_{12} as the density of component 2 becomes very low. As D_{12}^0 and D_1^0 stand in eq 3, their ratio is independent of temperature, but if a higher order Chapman−Enskog correction is made for D_{12}^0 and D_1^0, then the ratio may depend on temperature. However, such a correction is small at a relatively elevated temperature, and we will ignore it in this work.

In the tracer limit for species 2 where $X_2 \to 0$ the ratio of the tracer diffusion coefficient D_t for species 2 (the solute) to the solvent self-diffusion coefficient D_1 is approximately given by[3,8]

$$R_d \equiv \frac{D_t}{D_1} = \left(\frac{2}{1 + \sigma_2/\sigma_1}\right)^2\left[\frac{1}{2}\left(1 + \frac{m_1}{m_2}\right)\right]^{1/2} \tag{4}$$

Even though D_t and D_1 individually depend on temperature and density rather strongly, this ratio R_d is independent of density and temperature, but depends on the size ratio and the mass ratio only. The robustness of this constant ratio, rather its generalization to complex liquids, will be demonstrated in the following by extensively testing the generalized relation against experimental data. In this regard, it should be noted that the SE relation $\eta D_t = C(T)$ has a temperature-dependent coefficient. Because the ratio R_d can be readily measured in the laboratory, for example, by means of NMR methods, the size and mass ratio can be experimentally determined therewith. We remark that determination[9] of size parameters hitherto has not been possible in a way consistent with the intermolecular potential model chosen for the organic substances considered below.

Although the ratio R_d in eq 4 is based on the free volume theory of diffusion for simple liquids, we find that it remains still applicable to polyatomic (molecular) liquids, provided that the size ratio σ_2/σ_1 of the molecules is estimated from the van der Waals radius r_{wi} of species i, which is defined by $r_{wi} = (3V_{wi}/4\pi)^{1/3}$ with V_{wi} denoting the van der Waals volume, and the van der Waals volume is obtained by adding up the atomic increments available in the literature.[7,10] This procedure is made plausible by assuming that D_{12}^0 and D_1^0 are, respectively, the diffusion and self-diffusion coefficients of hypothetical gases with van der Waals radii r_{wi} ($i = 1, 2$) and thus replacing σ_2/σ_1 with r_{w2}/r_{w1}. Formula 4 therefore is, in effect, generalized to complex molecular liquids. The ratio now reads

$$R_d = \left(\frac{2}{1 + r_{w2}/r_{w1}}\right)^2\left[\frac{1}{2}\left(1 + \frac{m_1}{m_2}\right)\right]^{1/2} \equiv R_s \tag{5}$$

This relation is very simple and consequently has a high potential for applications to chemistry and biology because it can easily yield the information on the sizes of the solute and solvent molecules in solution, which are not trivial to acquire but quite useful. The crucial question is: is it reliable? It is also possible to use for determining D_t from D_1 and vice versa, provided r_{w2}/r_{w1} is known. The quality of the preceding relation between D_t and D_1 will be tested against experiment for various organic chemical systems in the following, and we find it robust on the basis of the systems examined, numbering about 60.

III. Materials and Methods of Measurement

Chemicals were obtained from EM Science (Cincinnati, OH) for methanol, Aldrich (Milwaukee, WI) for ethanol, Anachemia (Montreal, QC) for 1-propanol, American Chemicals (Montreal, QC) for acetone and cyclohexane, Mallinckrodt (Paris, KY) for hexane, BDH (Toronto, ON) for ethyl acetate, and Sigma (St. Louis, MO) for 1,2-propanediol and DMSO, respectively. All the solvents and tracers used in the present paper were analytical or HPLC grade and used without further purification. Benzene-d_6 (99.5%) was obtained from Sigma (St. Louis, MO) and used as received. For the tracer diffusion coefficient measurements in benzene, 1% (w/w) tracer solutions were prepared in benzene-d_6. The benzene self-diffusion coefficient was measured with 1% (w/w) benzene-h_6 in benzene-d_6 solution.

The diffusion measurements were carried out at 25 °C on a 300 MHz Bruker Avance AMX-300 NMR spectrometer, and the simple Stejskal-Tanner PGSE pulse sequence was used.[11] A Bruker magnetic resonance imaging probe, Micro 2.5 probe, was used in conjunction with a gradient amplifier (BAFPA-40). The gradient strength was calibrated with the one-dimensional image profile of a well-defined object in water solution containing a trace of $CuSO_4$. The calibration was checked with tracer H_2O in D_2O solution by measuring the self-diffusion coefficient of HDO at 25 °C (1.902×10^{-9}m^2/s). The measurements were done by increasing the gradient field strength, G, from 10 to 80 G/cm, and each diffusion coefficient was calculated typically with 15 points. The other parameters, which were optimized to each sample depending on the extent of echo attenuation, were kept constant: 90° pulse lengths (20 ms), gradient pulse length ($\delta = 0.5-1.1$ ms), and delay between two gradient pulses ($\Delta = 60$ ms) were those indicated in parentheses. The measurements of the diffusion coefficients by the method described are performed within about ±5% of error.

Echo attenuation can be expressed as the equation

$$I(2t) = I(0)\exp(-2\tau/T_2)\exp[-\gamma^2\delta^2G^2D(\Delta - \delta/3)] \tag{6}$$

where $I(2t)$ and $I(0)\exp(-2\tau/T_2)$ represent the echo intensities with and without the gradient pulses, τ is the delay between 90° and 180° pulses, T_2 is the spin−spin relaxation time, and γ is the magnetogyric ratio of the nucleus (2.675×10^{11} rad G^{-1} s^{-1} for ^{1}H). Once G is known, the logarithm of the echo intensity

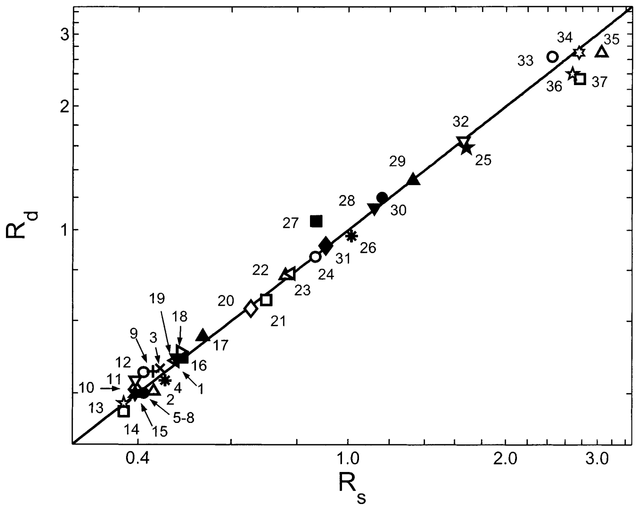

Figure 1. R_d vs R_s (size and mass ratio dependence of $R_d = D_t/D_1$) in the case of solvation effects assumed to be negligible. The solid line is the prediction by the present theory and the symbols are experimental results for R_d. The solvent for the tracer diffusion of **1**−**19** is water and the solute is benzene for **1**, toluene for **2**, aniline for **3**, phenol for **4**, *o*-cresol for **5**, *m*-cresol for **6**, *p*-cresol for **7**, 2-chlorophenol for **8**, chlorobenzene for **9**, 1,2-dichlorobenzene for **10**, 1,4-dichlorobenzene for **11**, bromobenzene for **12**, 1,2-dibromobenzene for **13**, 1,4-dibromobenzene for **14**, 3-nitrophenol for **15**, pyridine for **16**, acetone for **17**, DMSO for **18**, and 2-butanone for **19**, respectively. The solvent is acetone for **20**−**24** whereas the solute is propiophenone for **20**, acetophenone for **21**, chlorobenzene for **22**, toluene for **23**, and benzene for **24**, respectively. For **25**−**31**, the solvent is benzene whereas the solute is MeOH for **25**, EtOH for **26**, *n*-hexane for **27**, 1-PrOH for **28**, DMSO for **29**, acetone for **30**, and cyclohexane for **31**, respectively. For **32**−**37**, the solute is water whereas the solvent is: acetonitrile for **32**, benzene for **33**, toluene for **34**, *p*-xylene for **35**, cyclohexane for **36**, and *n*-hexane for **37**, respectively.

is plotted against the *b* value [$b = -\gamma^2\delta^2G^2(\Delta - \delta/3)$], and the diffusion coefficient *D* was derived from the slope of the plot. The diffusion coefficients from the literature are indicated by the reference from which they were obtained.

IV. Test of the Relation for R_d

We have applied formula 5 first to tracer diffusion where solvation effects may be assumed to be negligible. In Figure 1, the theoretical R_d vs R_s is shown in logarithmic scale in comparison with the experimental data for the tracer diffusion of a series of benzene derivatives in water (**1**−**19**) or in acetone (**20**−**24**), of some organic molecules in benzene (**25**−**31**), and of water in various solvents (**32**−**37**). The solid line is predicted by formula 5 and the various symbols represent the experimental data on D_t and D_1 available in the literature[12,13] or measured by Kwak and Lafleur.[14] The van der Waals radii[7,10] and R_s values computed therewith for various solutes in Figure 1 are given in Tables 1−3, where the experimental D_t values measured and employed for the calculation of R_d are also given. The temperature of measurement is $T = 298$ K for most cases, unless specified otherwise. Within about ±5% in deviation, which is comparable with the experimental uncertainties for the D_t and D_1 data, there appears to be a good agreement between the predictions of the theory and the experimental results. The deviations, however, are found to be larger for *n*-hexane (**27, 37**), being on the order of 10%.

TABLE 1: Tracer van der Waals Radii and Tracer Diffusion Coefficients in Water ($T = 298$ K)′

solute (Figure 1)	r_{w2}/Å	R_s	$10^9 D_t$/m^2 s^{-1}	D_t/D_1
benzene (**1**)	2.68	0.473	1.13[12a]	0.478
toluene (**2**)	2.87	0.428	0.93[12a]	0.404
aniline (**3**)	2.82	0.437	1.05[12b]	0.457
phenol (**4**)	2.77	0.447	1.00[12b]	0.434
o-cresol (**5**)	2.95	0.408	0.93[12b]	0.403
m-cresol (**6**)	2.95	0.408	0.89[12b]	0.387
p-cresol (**7**)	2.95	0.408	0.91[12b]	0.397
2-chlorophenol (**8**)	2.93	0.407	0.93[12b]	0.404
chlorobenzene (**9**)	2.84	0.427	1.04[12a]	0.452
1,2-dichlorobenzene (**10**)	2.98	0.395	0.94[12a]	0.409
1,4-dichlorobenzene (**11**)	2.98	0.395	0.99[12a]	0.430
bromobenzene (**12**)	2.88	0.411	1.03[12a]	0.448
1,2-dibromobenzene (**13**)	3.05	0.376	0.87[12a]	0.378
1,4-dibromobenze (**14**)	3.05	0.376	0.83[12a]	0.361
3-nitrophenol (**15**)	2.99	0.395	0.92[12b]	0.399
pyridine (**16**)	2.62	0.485	1.12[12b]	0.487
acetone (**17**)	2.49	0.533	1.28[12c]	0.556
DMSO (**18**)	2.64	0.481	1.41[14]	0.505 ($T = 310$ K)
2-butanone (**19**)	2.69	0.473	1.36[14]	0.487 ($T = 310$ K)

TABLE 2: Tracer van der Waals Radii and Tracer Diffusion Coefficients in Acetone or benzene ($T = 298$ K)′

solute (Figure 1)	r_{w2}/Å	R_s	$10^9 D_t$/m^2 s^{-1}	D_t/D_1
propiophenone (**20**)	3.18	0.653	3.08[12e]	0.644
acetophenone (**21**)	3.04	0.698	3.23[12e]	0.676
chlorobenzene (**22**)	2.84	0.760	3.71[12e]	0.776
toluene (**23**)	2.87	0.779	3.75[12e]	0.785
benzene (**24**)	2.68	0.866	4.12[12e]	0.862
MeOH (**25**)	2.05	1.68	3.30[14]	1.59
EtOH (**26**)	2.33	1.33	2.73[14]	1.32
n-hexane (**27**)	3.00	0.870	2.18[14]	1.05
1-PrOH (**28**)	2.56	1.12	2.35[14]	1.13
DMSO (**29**)	2.64	1.01	2.01[14]	0.971
acetone (**30**)	2.49	1.16	2.75[12c]	1.20
cyclohexane (**31**)	2.90	0.906	2.09[12c]	0.917

TABLE 3: Solvent van der Waals Radii and Tracer Diffusion Coefficients of Water ($T = 298$ K)′

solvent (Figure 1)	r_{w1}/Å	R_s	$10^9 D_t$/m^{2}s^{-1}	D_t/D_1
acetonitrile (**32**)	2.68	2.45	6.41[12d]	2.68 ($T = 303$ K)
benzene (**33**)	2.24	1.66	6.28[12d]	1.65 ($T = 303$ K)
toluene (**34**)	2.87	2.76	6.07[12g]	2.70
p-xylene (**35**)	3.03	3.05	5.62[12g]	2.70
cyclohexane (**36**)	2.90	2.68	3.40[12g]	2.40
n-hexane (**37**)	3.00	2.77	9.53[12g]	2.33

The situation becomes somewhat different from that for the systems considered in Figure 1 in the case of tracer diffusion in the solvents when solvation effects on solute molecules are far from being negligible, for example, owing to the hydrogen bonds formed. We take into account such effects for tracers with apparent hydrogen bonding capabilities in water by following the Edward method[7] of determining r_{w2}: this method assumes that a hydroxy group in a tracer molecule is bonded to one water molecule, which consequently gives rise to an increase of about 19 Å^3 in V_{w2} (see Table 4). In Figure 2 (see also Tables 4−6) the R_s values thus predicted by formula 5 are shown in comparison with the experimental results.[15,16] The agreement between theory and experiment is surprisingly good, especially, for 1-ROH in a series of alcohol tracers in water, where R stands for the aliphatic functional groups. It is interesting to observe that the diffusion of the polyols in water (**7**−**9**) shown in Figure 2 is well accounted for with an increase of V_{w2} by the amount of V_{w1} of one water molecule, contrary to the assertion[7] that one water molecule is bonded to each hydroxy group of a solute molecule—a polyol. In fact, the polyols of our data set can be divided into two categories in terms of the degree of hydration. On one hand, polyols such as ethylene glycol, glycerol, and pentaerythritol show very good agreement with the theoretical prediction when one hydration molecule is assumed. On the other hand, polyols such as 1,2-butanediol[17] (labeled **10s2** in Table 4), 1,2,6-hexanetriol[17] (labeld **10s3** in Table 4), and

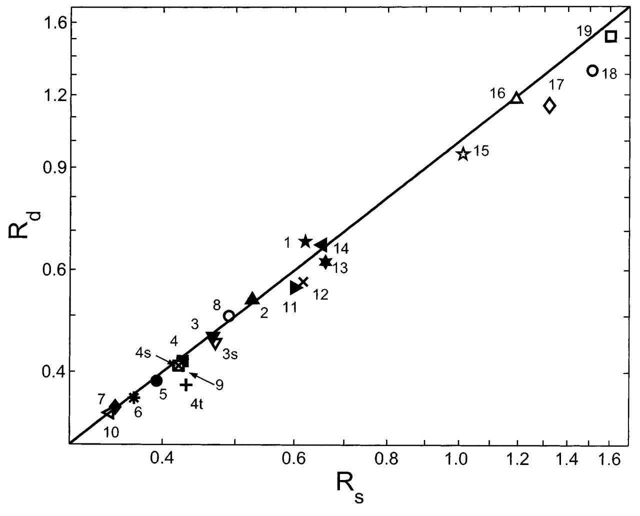

Figure 2. R_d vs R_s in the case of hydration effects present. The solid line is the prediction of the present theory and the symbols are experimental results for R_d. Water is the solvent for **1**−**10** whereas the tracers are MeOH for **1**, EtOH for **2**, 1-PrOH for **3**, 2-PrOH for **3s**, 1-BuOH for **4**, 2-BuOH and *i*-BuOH for **4s**, *t*-BuOH for **4t**, 1-pentanol for **5**, 1-hexanol for **6**, 1-heptanol for **7**, ethyleneglycol for **8**, gylcerol for **9**, and pentaerythritol for **10**, respectively. Acetone is the solvent for **11**−**14** whereas the solute is 2-chlorophenol for **11**, *p*-cresol for **12**, phenol for **13**, and aniline for **14**, respectively. For **15**−**19** water is the tracer in the solvent of MeOH for **15**, EtOH for **16**, acetone for **17**, DMSO for **18**, and ethyl acetate for **19,** respectively.

TABLE 4: van der Waals Radii and Tracer Diffusion Coefficients of Alcohols in Water (T = 298 K)′

solute (Figure 2)	r_{w2}/Å	R_s	$10^9 D_t$/m^2 s^{-1}	D_t/D_1
methanol (**1**)	2.36	0.603	1.54^{15a}	0.672
ethanol (**2**)	2.58	0.527	1.23^{15a}	0.533
1-propanol (**3**)	2.77	0.467	1.06^{15a}	0.460
2-propanol (**3s**)	2.77	0.467	1.03^{15a}	0.447
1-butanol (**4**)	2.93	0.425	0.96^{15a}	0.417
2-butanol (**4s**)	2.93	0.425	0.94^{15a}	0.409
iso-butanol (**4s**)	2.93	0.425	0.95^{15a}	0.413
tert-butyl alcohol (**4t**)	2.93	0.425	0.88^{15a}	0.381
1-propanol (**5**)	3.08	0.392	0.89^{15a}	0.386
1-hexanol (**6**)	3.22	0.366	0.83^{15a}	0.361
1-heptanol (**7**)	3.35	0.345	0.80^{15a}	0.348
ethyleneglycol (**8**)	2.67	0.487	1.14^{15b}	0.496
glycerol (**9**)	2.92	0.420	0.95^{15b}	0.411
pentaerythriotol (**10**)	3.32	0.343	0.78^{15b}	0.339
2-methyl-2,4-pentanediol (**10s1**)	3.41	0.336	0.75^{17}	0.324
1,2-butanediol (**10s2**)	3.16	0.379	0.86^{17}	0.375
1,2,6-hexanetriol (**10s3**)	3.46	0.327	0.76^{17}	0.328

TABLE 5: van der Waals Radii and Tracer Diffusion Coefficients in Acetone (T = 298 K)′

solute (Figure 2)	r_{w2}/Å	R_s	$10^9 D_t$/m^2 s^{-1}	D_t/D_1
2-chlorophenol (**11**)	3.44	0.602	2.66^{12e}	0.556
p-cresol (**12**)	3.45	0.616	2.74^{12e}	0.573
phenol (**13**)	3.32	0.660	2.93^{12e}	0.613
aniline (**14**)	3.36	0.653	3.17^{12e}	0.663

2-methyl-2, 4-pentanediol[17] (labeled **10s1** in Table 4) need two hydration molecules to get a good agreement with the theoretical prediction. A distinct feature between those groups is that each carbon atom in the first category contains a hydroxyl group. This aspect needs a further independent investigation to draw a more definite conclusion on the issue. However, one thing that should be mentioned is that in aqueous systems an increasing number of hydrogen bonding groups in a tracer does not always result in a retarded diffusion of the tracer.

TABLE 6: van der Waals Radii and Tracer Diffusion Coefficients of Water in Polar Solvents (T = 298 K)′

solvent (Figure 2)	r_{w2}/Å	R_s	$10^9 D_t$/m^2 s^{-1}	D_t/D_1
methanol (**15**)	2.38	1.01	2.19^{15c}	0.950
ethanol (**16**)	2.60	1.19	1.18^{15c}	1.18
acetone (**17**)	2.73	1.32	5.50^{12c}	1.15
DMSO(**18**)	2.86	1.51	0.90^{12g}	1.32
ethyl acetate (**19**)	2.96	1.60	4.25^{12g}	1.51

Tracer diffusion of **11**−**19** in organic solvents capable of forming hydrogen bonds with the tracer molecules is also shown in Figure 2 to demonstrate the solvation effect expected to occur in a way similar to the alcohol diffusion in water. In determining r_{w2}, the V_{w2} has been increased from its "naked state" value by as much as V_{w1} of one solvent molecule (see Tables 5 and 6). The overall correlation between R_s and R_d seems to be reasonable despite about 10% deviations observed for the water diffusion in acetone (**17**) and in DMSO (**18**). The reason for such discrepancy, however, is not clear at present. It should be noted that no such solvation effects are considered in the case of ketones as a solute, as is evident in Figure 1 (e.g., **17** and **19** in water and **20** and **21** in acetone). This is because ketones as a solvent can accommodate hydrogen bonds but only in their enol forms. However, the enol concentration is usually in trace amount ([enol]/[ketone] ~ 10^{-7}). Therefore, if the ketone is a solute, there is an insufficient number of enol forms of the ketone to form hydrogen bonds with the solvent molecules so as to contribute to the hydrogen bonding effects to a noticeable degree.

V. Conclusion

In this paper we have presented a simple linear relation holding between the tracer diffusion and self-diffusion coefficients of polyatomic liquids. The ratio $R_d = D_t/D_1$ is independent of temperature and density and depends on only the size and mass ratios of the solvent and solute molecules. When the size ratio is estimated by using the van der Waals radii of the constituent molecules, the formula for R_d excellently accounts for the experimental results for the systems considered. The systems examined include those in which hydrogen bonding effects on solute diffusion are present. The method of estimating the size ratio is validated by testing the formula for a large number of systems, approximately 60 in number. The $R_d = D_t/D_1$ formula appears to be an excellent means of estimating molecular sizes and should be applicable to a variety of purposes in chemistry and biochemistry. The formula is not restricted to a particular range of size ratio of the solute and solvent molecules unlike the SE relation that assumes the tracer particle to be much larger than the solvent (medium) molecule in diameter, so that a continuum treatment of the medium is justified. Because this assumption is hardly satisfied by the systems considered in this work, the SE relation is not expected to be useful for them. Another molecular theory implication of the validation of R_d vs R_s made in this work is that diffusions of polyatomic molecules in a complex solvent may be treated by a statistical mechanics method, namely, the free volume theory, by assuming they are rigid spherical molecules whose radius may be estimated with their van der Waals volume according to the procedure described in this paper. This implication is rather intriguing and seems to be worth further exploration at the level of nonequilibrium statistical mechanics. On the experimental side, through this work we have gained another piece of rather convincing evidence that the NMR techniques can provide reliable diffusion coefficients that enable us to estimate other transport coefficients (e.g., viscosity and thermal conductivity) through the relations derived from statistical mechanics and reported in the literature.

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(13) In Figure 1 the experimental data for D_1 (10^{-9} m^2 s^{-1}) of water used for **1**−**19** at $T = 298.15$ K is 2.30 from ref 12h. The value of 4.78 for D_1 of acetone used for **20**−**24** is an average taken from refs 12c and 12d. The D_1 of C_6H_6 used are 2.28 from ref 12c for **30** and **31** at 298 K and 2.39 from ref 12f for **32** at $T = 303$ K, respectively. The D_1 value for acetonitrile used at $T = 303$ K is 3.81 from ref 12f.

(14) The D_t data for **25**−**29** and the D_1 for **34**−**37** in Figure 1 were measured with the uncertainty of about ±5% by Kwak and Lafleur by using a pulsed magnetic field gradient NMR method at $T = 298$ K, whereas 2.79 for D_1 of water and 1.41 and 1.36 for D_t of **18** and **19**, respectively, were measured at $T = 310$ K. The measured D_t values are 2.25 for toluene, 2.08 for *p*-xylene, 1.42 for cyclohexane, and 4.08 for *n*-hexane, respectively. All the data used for **25**−**29** were measured in C_6D_6 at about 1% of solute mass fraction, including 2.07 as for D_1 of benzene.

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