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Effects of molecular association on mutual diffusion: A study of hydrogen bonding in dilute solutions

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Diffusivities of pseudoplanar molecules at trace concentration in methanol have been measured at 298.2 K using Taylor's dispersion method. The data of the polar and nonpolar aromatic solutes are compared, and the effects due to solute–solvent interactions on diffusion, together with the solvation numbers, are determined. In this study, the effects are combined with the recently developed solute hydrogen-bond scales to unravel hydrogen bonding between solute and solvent. It is found that the degrees of association of the solutes with methanol decrease in the sequence hydroquinone>aromatic acids>phenols>aromatic amines>aprotic aromatic compounds. Except for *o*-nitrophenol, which is capable of intramolecular hydrogen bonding, all aromatic acids, phenols, and amines studied behave more as hydrogen-bond donor than acceptor in methanol. The present work also indicates that motions of associated molecules can be understood in terms of the molecular behavior of nonassociated solutes and the hydrogen-bond acidity/basicity of polar solutes. © *1999 American Institute of Physics.* [S0021-9606(99)52306-4]

I. INTRODUCTION

Hydrogen bonding has long been a subject of intensive research efforts because of its importance in chemical and biological systems. Current research problems such as self-assembly[1] and molecular recognition[2] are largely connected with hydrogen bonding. Although experimental and theoretical publications on hydrogen bonding abound,[3] however, our understanding of this molecular phenomenon in dilute solutions is still in its relative infancy. Recently, there has been a considerable amount of interest in the study of the role that hydrogen bonding plays in solvation.[4–9] In previous work,[10,11] we developed a method of using diffusion measurements to determine the relative strength of hydrogen bonding and the number of solvent molecules associated with an aromatic solute containing one polar functional group in dilute solution. This method, however, is unable to provide more insights into the solute–solvent interactions. For example, in the case where both solute and solvent molecules are capable of being hydrogen-bond-donor (HBD) and hydrogen-bond-acceptor (HBA),[12] the solvation number calculated by this method cannot differentiate whether hydrogen bonding is due exclusively to a particular type of donor–acceptor pairing or whether it is a result of a mixture of both types of interactions existing between solute and solvent molecules in the solution. In the latter case, it is also of interest to find out quantitatively the extent to which each type of donor–acceptor pairing occurs. Nonetheless, complex hydrogen bonding in very dilute solution is still difficult to study by current experimental methods, and it appears that investigations of this kind have not been reported in the literature.

In another recent paper,[13] we showed that the limiting mutual diffusion coefficient of a solute capable of hydrogen bonding with acetone at one site can be described in terms of the diffusivity of a nonassociated solute with similar monomer size and shape and the 1:1 solute–solvent interaction energy determined from *ab initio* molecular orbital calculations. The relationship is as follows:

$$1/D_{12}^A = 1/D_{12}^N + \Delta D_{12}^{-1}, \tag{1}$$

where D_{12}^A is the diffusivity of an associated solute, D_{12}^N is the diffusivity of a similar nonassociated solute, and ΔD_{12}^{-1} is the excess reciprocal diffusivity (i.e., the difference between $1/D_{12}^A$ and $1/D_{12}^N$), which is a function of 1:1 solute–solvent interaction energies. For complex systems where hydrogen bonds are possibly formed (and broken) at multisites in different (unknown) proportions, however, solute–solvent interaction energies are difficult to be evaluated by *ab initio* molecular orbital calculations. In the present paper, we demonstrate that ΔD_{12}^{-1} is also related to the recently developed molecular scales[14] of overall hydrogen-bond acidity ($\Sigma \alpha^H$) and basicity ($\Sigma \beta^H$), which are the relative hydrogen-bond-donating and -accepting tendencies obtained from linear free-energy relationship (LFER). Details of the construction of the scales have been reviewed by Abraham.[15] The main objective of this work is to obtain a better understanding of the molecular dynamics of associated molecules and the nature of hydrogen bonding, in particular the relative behavior of solutes as HBD and HBA, in dilute solutions. The approach is via the study of the effects of molecular association on mutual diffusion.

II. EXPERIMENT

Mutual diffusion coefficients at infinite dilution were measured by the Taylor dispersion method, known also as the chromatographic peak-broadening technique. In this

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method, a small sample of a dilute solution is injected into a stream of solvent in a capillary tube. Taylor[16] has shown that for a laminar flow, the combination of flow and diffusion results in a Gaussian distribution of solute along the tube. The diffusion coefficient for liquids can be determined from the equation[17]

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

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

The experimental setup and procedures for measurements of mutual diffusion coefficients were similar to those described previously.[13] Briefly, the diffusion tube was an 85.7 m length of 304 stainless-steel tube of 1.59 mm o.d. and 0.98 mm i.d. The capillary tubing was coiled in a 40 cm-diameter circle and placed in a constant-temperature bath which was controlled to 298.15 ± 0.02 K. A 50 μL sample of a dilute ($\sim$1% concentration by weight) solution was injected through an injection valve (Rheodyne, model 7725) into the solvent stream. To ensure laminar flow, the solvent flow rate was adjusted so that the constant volume flow was only between 0.1 and 0.2 $cm^3 min^{-1}$. In this work, the solvent was delivered by a Bio-Rad HPLC pump (model 1350) with a flow rate precision of $\pm$0.1%. At the end of the diffusion tube, the solute dispersion peak was detected with a Dynamax differential refractometer (model RI-1) with output to a chart recorder.

In the present study, the solute mesitylene (98%, Riedel-de Haen) was purified by fractional distillation; benzene (99.9% +, Aldrich), chlorobenzene (99.9% +, Aldrich), toluene (99.5%, E. Merck), ethylbenzene (99% +, BDH), naphthalene (99% +, BDH), n-propylbenzene (99%, Fluka), 1-methylnaphthalene (98% +, Aldrich), biphenyl (99% +, Koch-Light), hydroquinone (99% +, Aldrich), o-nitrophenol (99% +, E. Merck), p-nitrophenol (99.5% +, E. Merck), p-chlorobenzoic acid (99%, Aldrich), p-methylbenzoic acid (99% +, E. Merck), phenol (99.5%, E. Merck), o-cresol (99% +, E. Merck), p-cresol (99% +, Fluka), 1-naphthol (99% +, Aldrich), 2-naphthol (99%, Aldrich), aniline (99.5%, Aldrich), p-chloroaniline (99% +, Fluka), m-toluidine (99% +, E. Merck), p-toluidine (99.9%, Aldrich), benzaldehyde (99% +, E. Merck), o-toluadehyde (98% +, E. Merck), nitrobenzene (99% +, Aldrich), o-nitrotoluene (99% +, E. Merck), acetophenone (99%, Aldrich), m-methylacetophenone (98% +, Aldrich), benzonitrile (99% +, E. Merck), and benzl cyanide (99% +, E. Merck) were used as received. All solutes are pseudoplanar aromatic compounds with similar shape; the structures of the polar solutes studied are shown in Fig. 1. The solvent methanol (99.9% +, Aldrich) was degassed before use by ultrasonic bath. At least three measurements were made to obtain a diffusion coefficient. All data were recorded at 298.15 ± 0.02 K, with temperature measured using a Beckmann thermometer calibrated with a certified thermometer (Baird and Tatlock, No. GDZ27736). The precision of our data was generally within $\pm$1%.
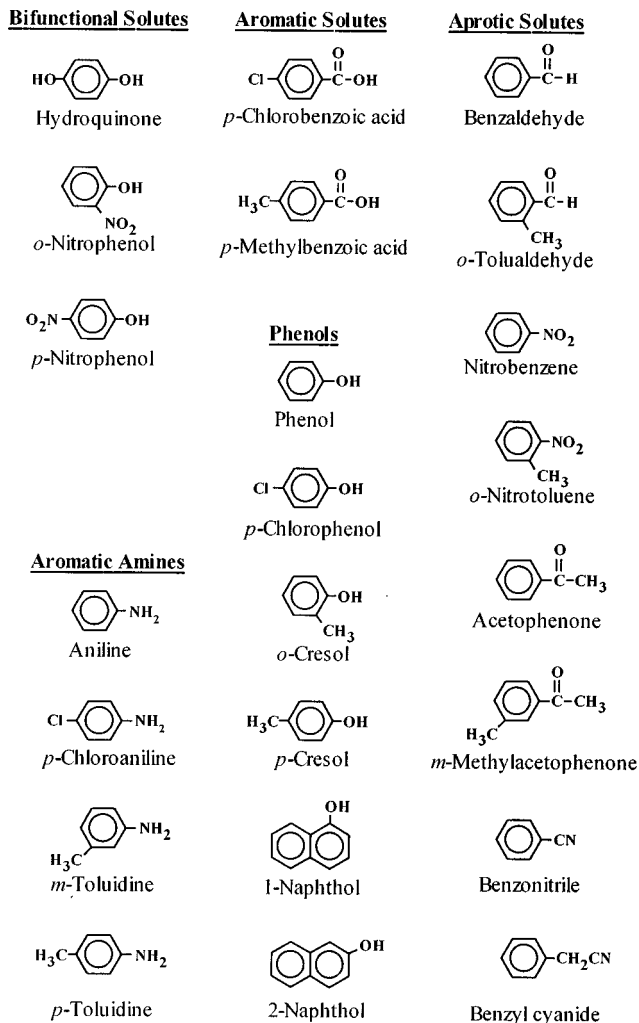

FIG. 1. Structures of the polar aromatic solutes investigated.

III. RESULTS AND DISCUSSION

For nonassociated solutes with similar shape diffusing in a given solvent, we have recently observed[18] from experimental measurements at constant temperature that

$$1/D_{12}^N = kV + c, \qquad (3)$$

where D_{12}^N refers to the limiting mutual diffusivity of nonassociated solutes, k and c are constants, and V represents the molecular volume of solutes. In the above study, Eq. (3) has been demonstrated to be applicable for solutes ranging from 80 to 320 $Å^3$ in size. Table I shows the literature values of limiting mutual diffusion coefficient of pseudoplanar solutes in acetone at 298.2 K. Also presented in the table are the van der Waals (VDW) volume and the hydrogen-bond acidity of solutes. For the nonassociated solutes in acetone, a linear relationship was indeed found between the reciprocal of diffusivity and the molecular volume of the solutes.[13] The relationship at 298.2 K can be represented by the following expression:

$$(D_{12}^N)^{-1}/10^9 \ \ m^{-2} s = 1.41 \times 10^{-3} V/Å^3 + 0.131, \qquad (4)$$

where D_{12}^N is the limiting mutual diffusion coefficient and V is the van der Waals volume of the nonassociated solutes.

TABLE I. Limiting mutual diffusion coefficients of pseudoplanar solutes in acetone at 298.2 K.

	VDW vol/Å^3 [a]	$D_{12}^N/10^{-9}$ m^2 s^{-1}	$D_{12}^A/10^{-9}$ m^2 s^{-1}	Cal $D_{12}^N/10^{-9}$ m^2 s^{-1}	$\Sigma \alpha_2^{\text{H}}$ [f]	Cal'd $D_{12}^A/10^{-9}$ m^2 s^{-1}
Nonassociated solutes						
Benzene	81.1	4.07 ± 0.04[b]		4.07	0.00	
Chlorobenzene	97.2	3.71 ± 0.03[b]		3.73	0.00	
Toluene	97.6	3.75 ± 0.03[b]		3.72	0.00	
Ethylbenzene	113.8	3.45 ± 0.02[b]		3.43	0.00	
Naphthalene	125.4	3.25 ± 0.03[b]		3.25	0.00	
1,2,4-Trichlorobenzene	129.3	3.13 ± 0.03[b]		3.19	0.00	
Propylbenzene	130.0	3.24 ± 0.03[b]		3.18	0.00	
Mesitylene	130.7	3.16 ± 0.03[c]		3.17	0.00	
Biphenyl	152.4	2.89 ± 0.03[b]		2.89	0.00	
Aromatic acid						
Benzoic acid	109.0		2.62[d]	3.51	0.59	2.66
Phenols						
Phenol	89.6		2.93 ± 0.03[c]	3.88	0.60	2.86
p-Chlorophenol	105.7		2.66 ± 0.03[c]	3.57	0.67	2.61
p-Cresol	106.2		2.72 ± 0.03[c]	3.56	0.57	2.71
1-Naphthol	133.9		2.44 ± 0.02[c]	3.12	0.61	2.41
2-Naphthol	133.9		2.41 ± 0.02[c]	3.12	0.61	2.41
Aromatic amines						
Aniline	93.8		3.17 ± 0.04[e]	3.80	0.26	3.29
p-Chloroaniline	109.9		2.92 ± 0.03[e]	3.49	0.30	3.00
p-Toluidine	110.4		2.94 ± 0.03[e]	3.48	0.23	3.10

[a]The values are averages from Refs. 19–22.
[b]From Ref. 18.
[c]From Ref. 13.
[d]From Ref. 23.
[e]From Ref. 10.
[f]From Ref. 14.

Equation (4) fits all data within 1.9%, and the correlation coefficient is 0.996. Table I also shows the calculated values of D_{12}^N from Eq. (4) for all solutes at their monomer's van der Waals volume for comparison. For solutes capable of associating with solvent molecules, ΔD_{12}^N in Eq. (1) can thus be obtained by subtracting $1/D_{12}^N$ from the experimental value of $1/D_{12}^A$. Since acetone can act only as an HBA, it is reasonable to apply the framework Eq. (1) such that ΔD_{12}^{-1} is not only a function of the 1:1 solute–solvent interaction energy as previously reported,[13] but alternatively also proportional to $\Sigma \alpha^{\text{H}}$ (the relative hydrogen-bond-donating ability) of solutes. A plot of ΔD_{12}^{-1} vs $\Sigma \alpha^{\text{H}}$ for all solutes is displayed in Fig. 2. In fact, all values of ΔD_{12}^{-1} were fitted fairly well by the following equation with only one parameter:

$$\Delta D_{12}^{-1}/10^9 \ \text{m}^{-2}\text{s}=0.154\Sigma \alpha^{\text{H}}. \tag{5}$$

The standard deviation of the fit is 9.67×10^{-3}. When Eq. (4) and Eq. (5) are substituted into Eq. (1), all values calculated for D_{12}^A agree with the experimental values within 5.5%, the average deviation being only 2.2%. The calculated D_{12}^A values are also listed in Table I.

The above results encouraged us to further investigate correlation between ΔD_{12}^{-1} and the overall solute hydrogen-bond scales for other systems, and to use it for probing complex hydrogen bonding, in particular between polar solute and protic solvent. Table II lists the limiting mutual diffusion coefficients of some nonassociated aromatic compounds in

methanol at 298.2 K. A linear relationship between the reciprocal of diffusivity and the molecular volume of the solutes was obtained as follows:

$$(D_{12}^N)^{-1}/10^9 \ \text{m}^{-2}\text{s}=2.30\times10^{-3}V/\text{Å}^3+0.193. \tag{6}$$

Equation (6) fits all data within 1.6%, and the correlation coefficient is 0.997. The linear regression line is shown in Fig. 3. The relevant data for solutes capable of association with methanol are given in Table III. The effects of solute–solvent interactions on diffusion are presented as deviations
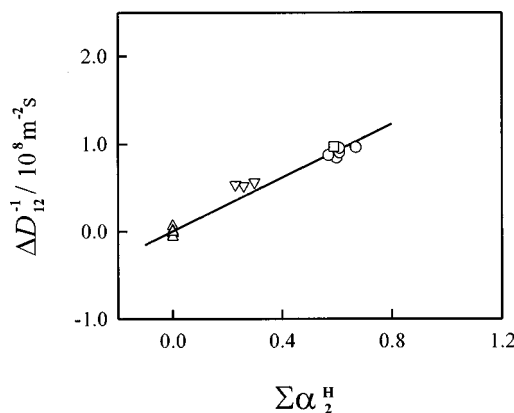

FIG. 2. Variation of ΔD_{12}^{-1} with hydrogen-bond acidity of solutes in acetone at 298.2 K: ($\triangle$) nonassociated solutes, ($\triangledown$) aromatic amines, ($\bigcirc$) phenols, and ($\square$) benzoic acid.

TABLE II. Limiting mutual diffusion coefficients of nonassociated pseudoplanar solutes in methanol at 298.2 K.

	VDW vol/Å^{3} [a]	$D_{12}^N/10^{-9}$ m^2 s^{-1}
Benzene	81.1	2.61±0.02
Chlorobenzene	97.2	2.40±0.02
Toluene	97.6	2.42±0.02
Ethylbenzene	113.8	2.23±0.01
Naphthalene	125.4	2.08±0.02
Propylbenzene	130.0	2.06±0.01
Mesitylene	130.7	2.02±0.01
1-Methynaphthalene	141.9	1.90±0.02
Biphenyl	152.4	1.85±0.02

[a]The values are averages from Refs. 19–22.

FIG. 3. Variation of $1/D_{12}$ with molecular volume of solutes diffusing in methanol at 298.2 K: (▲) nonassociated solutes, (●) hydroquinone, (◆) p-nitrophenol, (■) o-nitrophenol, (□) aromatic acids, (○) phenols, (▽) aromatic amines, and (◇) aprotic solutes.

(ΔD_{12}^{-1}) from the ''nonassociated'' line in Fig. 3. The effects vary from relatively small for aprotic solutes to a large 92% in the case of hydroquinone. In this study, the decrease in D_{12} of the polar compounds cannot be attributed to solute–solute interactions, as the solutions are very dilute and methanol is polar.

The degrees of association of solutes with solvent can be revealed from the solvation numbers, which are found by considering in the diffusion process that a polar solute is diffusing to a certain extent as a solute–solvent complex instead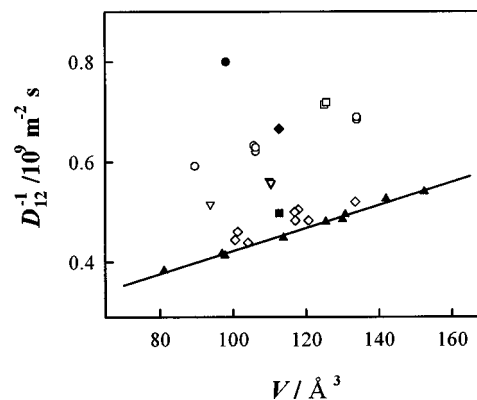 of only as a monomer. The average size increase of a polar solute due to hydrogen bonding can actually be evaluated from ΔD_{12}^{-1}. This is equivalent to the increase in the van der Waals volume that produces such an amount of $1/D_{12}$ deviation on the nonassociated line. The solvation number n, which is the average number of methanol molecules associated with a solute in this study, can be calculated by dividing the solute volume increased by the van der

TABLE III. Limiting mutual diffusion coefficients, solvation numbers (n), and percent HBA/HBD of associated pseudoplanar solutes in methanol at 298.2 K.

	VDW vol/Å^{3} [a]	$D_{12}^A/10^{-9}$ m^2 s^{-1}	Cal $D_{12}^N/10^{-9}$ m^2 s^{-1}	$\Sigma\alpha_2^{H}$ [c]	$\Sigma\beta_2^{H}$ [c]	Cal $D_{12}^A/10^{-9}$ m^2 s^{-1}	n	%A	%B
Bi-functional solutes									
Hydroquinone	98.1	1.25±0.01	2.39	1.16	0.60	1.25	4.8±0.4	88±4	12±2
o-Nitrophenol	112.6	2.01±0.02	2.22	0.05	0.37	2.02	0.6±0.1	33±2	67±11
p-Nitrophenol	112.6	1.50±0.02	2.22	0.82	0.26	1.42	2.6±0.2	92±4	8±2
Aromatic acids									
p-Chlorobenzoic acid	125.1	1.40±0.02	2.08	0.63	0.27	1.47	2.9±0.2	89±4	11±2
p-Methylbenzoic acid	125.6	1.39±0.01	2.08	0.60	0.38	1.46	3.0±0.2	85±4	15±3
Phenols									
Phenol	89.6	1.69±0.02[b]	2.51	0.60	0.30	1.68	2.4±0.2	88±4	12±2
p-Chlorophenol	105.7	1.58±0.01	2.30	0.67	0.20	1.56	2.5±0.2	92±4	8±2
o-Cresol	106.2	1.61±0.02	2.30	0.52	0.30	1.64	2.3±0.2	86±4	14±3
p-Cresol	106.2	1.59±0.01[b]	2.30	0.57	0.31	1.60	2.4±0.2	87±4	13±3
1-Naphthol	133.9	1.46±0.01	2.00	0.61	0.37	1.42	2.3±0.2	86±4	14±3
2-Naphthol	133.9	1.45±0.01	2.00	0.61	0.40	1.42	2.4±0.2	85±4	15±3
Aromatic amines									
Aniline	93.8	1.94±0.02[b]	2.45	0.26	0.41	1.94	1.4±0.1	70±3	30±5
p-Chloroaniline	109.9	1.78±0.01[b]	2.25	0.30	0.31	1.80	1.5±0.1	78±3	22±4
m-Toluidine	110.4	1.80±0.02	2.24	0.23	0.45	1.83	1.4±0.1	65±3	35±6
p-Toluidine	110.4	1.79±0.02[b]	2.24	0.23	0.45	1.83	1.4±0.1	65±3	35±6
Aprotic solutes									
Benzaldehyde	101.3	2.17±0.02	2.35	0	0.39	2.19	0.5±0.1	0	100
o-Tolualdehyde	117.9	1.98±0.02	2.16	0	0.40	2.02	0.6±0.1	0	100
Nitrobenzene	104.1	2.28±0.02	2.32	0	0.28	2.20	0.1±0.1	0	100
o-Nitrotoluene	120.7	2.07±0.02	2.13	0	0.27	2.04	0.2±0.1	0	100
Acetophenone	117.0	2.07±0.02	2.17	0	0.48	2.00	0.3±0.1	0	100
m-Methylacetophenone	133.5	1.92±0.02	2.00	0	0.49	1.86	0.3±0.1	0	100
Benzonitrile	100.6	2.25±0.02	2.36	0	0.33	2.23	0.3±0.1	0	100
Benzyl cyanide	116.8	2.00±0.02	2.17	0	0.45	2.02	0.5±0.1	0	100

[a]The values are averages from Refs. 19–22.
[b]From Ref. 10.
[c]From Ref. 14.
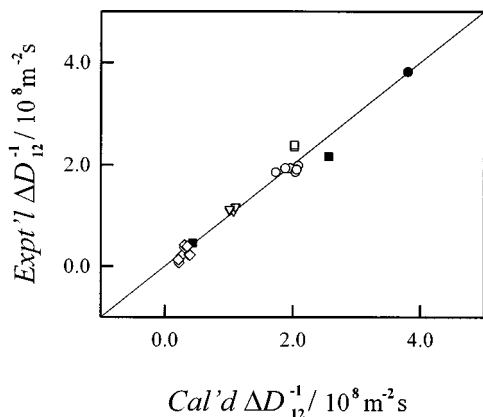
FIG. 4. Comparisons between experimental and calculated values of ΔD_{12}^{-1}: ($\diamond$) aprotic solutes, ($\triangledown$) aromatic amines, ($\bigcirc$) phenols, ($\square$) aromatic acids, ($\bullet$) hydroquinone, and ($\blacksquare$) nitrophenols.

Waals volume (34.8 Å^3) of the methanol monomer. The solvation numbers thus determined for the polar solutes, together with their estimated errors, are also given in Table III. It is noteworthy that for solutes containing the same polar group (e.g., the phenols), the solvation numbers are approximately equal. This indicates that the degree of association is mainly dependent on the type of polar group attached. From Table III, the degrees of association of solutes with methanol through hydrogen bonding decrease in the sequence hydroquinone>aromatic acids>phenols>aromatic amines>aprotic aromatic compounds. It should be noted that all aprotic aromatic solutes studied are only weakly associated with methanol, which may be due to their lack of hydrogen-bond-donating nature. Also, it is interesting that the values of n for hydroquinone and p-nitrophenol are nearly additive, i.e., they are contributed from each polar group with $-$OH$=2.4$ (see n for phenols) and $-$NO$_2=0.1$ (see n for nitrobenzene).

Unlike acetone, methanol can act as both an HBD and an HBA, and therefore ΔD_{12}^{-1} for the associated solutes can be considered as having two contributions from different interactions as follows:

$$\Delta D_{12}^{-1} = \mathbf{A} + \mathbf{B}. \tag{7}$$

In Eq. (7), $\mathbf{A}$ is proportional to solute (HBD)–solvent (HBA) interactions, and $\mathbf{B}$ is contributed from solute (HBA)–solvent (HBD) pairing, i.e., $\mathbf{A} \propto \Sigma \alpha_2^H \Sigma \beta_1^H$, and $\mathbf{B} \propto \Sigma \beta_2^H \Sigma \alpha_1^H$ where subscripts 1 and 2 denote solvent and solute, respectively. For dilute solution in methanol, the acidity and basicity of the solvent can be considered constant, and Eq. (7) can be rewritten as

$$\Delta D_{12}^{-1} = a \Sigma \alpha_2^H + b \Sigma \beta_2^H, \tag{8}$$

where a and b are constants at a given temperature. Equation (8) with $a=0.287\pm0.010$ and $b=0.079\pm0.013$ fits all $\Delta D_{12}^{-1}/10^9$ m^{-2} s in Table III within 0.04 units, and comparisons between the experimental and calculated values of ΔD_{12}^{-1} are shown in Fig. 4. The agreements are reasonable in consideration of the experimental error (ca. 1%) of the diffusion data and the uncertainty (ca. 0.03 units) in the $\Sigma \alpha_2^H$ and $\Sigma \beta_2^H$ values. In this study, $\Sigma \alpha_2^H$ varies from 0.00 to 1.16,

and $\Sigma \beta_2^H$ from 0.20 to 0.60. Similar to the case of acetone, the calculated D_{12}^A values are listed in Table III. The values are obtained by substituting Eqs. (6) and (8) into Eq. (1). All calculated values of D_{12}^A agree with the experimental values within 5.7%, the average deviation being only 2.1%. It should be noted that o-nitrophenol and p-nitrophenol are two isomers with similar size, mass, and shape. Nonetheless, their diffusivities as shown in Table III differ by 34%. Remarkably, our model above indeed predicts the large diffusivity difference between the two isomers. The good agreement between experimental and calculated values of D_{12}^A supports our model, and indicates that the diffusion behavior of associated molecules can be understood in terms of the general diffusion behavior of nonassociated molecules and the relative hydrogen-bond-donating and -accepting properties of solutes. Also shown in Table III are the calculated relative contributions of $\mathbf{A}$ and $\mathbf{B}$ to ΔD_{12}^{-1} as calculated from the fit of Eq. (8). Since $\mathbf{A}$ is the effect due to solute acting as an HBD and $\mathbf{B}$ from solute as an HBA, the values in Table III suggest that hydroquinone, aromatic acids, and phenols predominantly act as HBDs in methanol, although these molecules also perform as HBAs to the extent of about 8%–15%. For aromatic amines, our results show that these compounds behave on average ca. 70% as HBDs and ca. 30% as HBAs. It is of interest to note that o-nitrophenol acts mainly as an HBA instead (67% as an HBA and only 33% as an HBD), whereas the isomer p-nitrophenol is 92% HBD. Clearly, intramolecular hydrogen bonding in o-nitrophenol restricts its proton to form an intermolecular hydrogen bond with methanol. In general, it appears that a solute's ability of being HBD rather than HBA is more important in determining ΔD_{12}^{-1} or the degree of solute–solvent association in methanol.

IV. CONCLUSION

We have demonstrated in this work that the effects of hydrogen bonding on diffusion can be correlated with the scales of hydrogen-bond acidity and basicity, and that experimental diffusion data can be used to yield useful information concerning hydrogen bonding in dilute solution. For solutes containing one polar group, the degrees of solute-methanol association decrease in the sequence aromatic acids>phenols>aromatic amines>aprotic aromatic solutes, and all aromatic acids, phenols, and amines studied act mainly as hydrogen-bond donors in methanol. For solutes capable of hydrogen bonding at multisites, the existence of intramolecular hydrogen bonding can weaken the HBD capability of solutes as well as the intermolecular interactions with solvent. Our data generally indicate that the degree of solute–solvent association in methanol is largely dependent on a solute's ability as HBD, while HBA plays only a minor role. More importantly, we have presented a model here that can successfully predict diffusivities of associated molecules in methanol. Here, the implication is that theories for motions of associated molecules may possibly be built upon those for nonassociated ones (e.g., the rough–hard-sphere

theory) in terms of the strength of association or the relative hydrogen-bond-donating and -accepting properties of molecules.

[1] See, for example (a) A. Bhattacharya, S. D. Mahanti, and A. Chakrabarti, J. Chem. Phys. **108**, 10281 (1998); (b) D. M. Rudkevich and J. Rebek, Jr., Angew. Chem. Int. Ed. Engl. **36**, 846 (1997); (c) L. R. MacGillivray, R. H. Groeneman, and J. L. Atwood, J. Am. Chem. Soc. **120**, 2676 (1998); (d) R. Goetz and R. Lipowsky, J. Chem. Phys. **108**, 7397 (1998).

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