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The effects of molecular association on mutual diffusion in acetone

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Limiting mutual diffusion coefficients of aromatic compounds in acetone have been measured at 298.2 K by using the chromatographic peak-broadening method. The data of the polar and nonpolar pseudoplanar solutes are compared, and the effects of molecular association on diffusion as well as the solvation numbers are determined. It is found that the effects of hydrogen bonding are such that $-\text{OH} > -\text{NH}_2 > -\text{SH}$, and that the solvation numbers are approximately equal for solutes containing the same polar group. Using *ab initio* molecular orbital theory, molecular solute–acetone interaction energies have been calculated. There exists a nearly linear relationship between the interaction energy and the effect of solute–solvent association on diffusion. The applicability of the rough-hard-sphere theory to the diffusion of associated molecules is discussed. © 1997 American Institute of Physics. [S0021-9606(97)53330-7]

I. INTRODUCTION

Diffusion has long been a subject of intensive research efforts because of its importance in chemical and biological systems. Traditionally, diffusion in liquids has been discussed in terms of the hydrodynamic theory represented by the Stokes–Einstein equation. According to that equation, diffusion coefficients are dependent on solute radius, solvent viscosity, temperature, and a hydrodynamic frictional coefficient. Although the Stokes–Einstein equation describes the diffusion behavior of large spherical solutes fairly well, it nevertheless fails completely for solute molecules small in size compared to the solvent molecules.^{1–4} Recently, there has been a great deal of interest^{5–36} in the use of the rough-hard-sphere (RHS) theory^{37,38} for the interpretation of diffusion data. Based on the van der Waals (VDW) picture of condensed matter, the RHS theory assumes that motions of molecules in a liquid are determined primarily by the size and shape of the molecules (i.e., the short-range repulsive intermolecular forces); weak dipole–dipole interactions and other attractive forces which vary slowly in space play only a minor role. For limiting mutual diffusion, the RHS theory predicts diffusivities by the relation^{24,35,36}

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

where D_{12}^{RHS} is the limiting mutual diffusion coefficient, n_2 represents the number density of the solvent, σ_1 and σ_2 are the molecular diameters of solute and solvent, respectively, μ refers to the reduced mass of solute and solvent molecules, A_{12} is 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 account of the correlated molecular motions. Details of the VDW picture and the RHS theory have been reviewed by Chandler *et al.*³⁹ In general, the RHS theory accounts satisfactorily for the diffusion of nonassociated solutes. For molecules with strong intermolecular interactions, however,

it appears that our knowledge of the transport properties of liquids is still rather rudimentary. Nonetheless, molecular associations occur commonly in real liquid systems.

Investigations on the effects of molecular association on mutual diffusion are relatively few reported in the literature. This is probably because such effects are difficult to ascertain and quantify by current experimental methods. Previously, Longworth⁴⁰ and Tyrrell *et al.*⁴¹ have found that the hydrodynamic friction coefficients are different for polar solutes that can form hydrogen bonds with water and propan-1,2-diol, respectively. As mentioned above, however, the Stokes–Einstein equation as applied in these studies may not be valid and applicable at the molecular scale. Eastaer and Woolf⁴² have shown evidence of the effects of solute–solvent interaction on diffusion in water and octamethylcyclotetrasiloxane. Unfortunately, their study has not taken into account the effects of solute shape on diffusion. Such effects have been shown⁶ as large as 26% in the case of *n*-tetradecane as solvent. Recently, Akgerman *et al.*⁸ have extracted from experimental data the combined effects of hydrogen bonding and translational–rotational coupling. Nonetheless, they were unable to separate the effects of molecular association from the effect of coupling.

In this laboratory, we have a continuous interest in the experimental study of various molecular effects on diffusion. Previously, we have reported^{18,19} that diffusivities are insensitive to the mass and dipole moment of the solute molecules. In recent papers,⁶ we have demonstrated that a linear relationship exists between the reciprocal of the limiting mutual diffusion coefficients ($1/D_{12}$) of the nonassociated solutes with similar shape and the molecular volume (V) of the solutes. More recently, we have shown⁴³ that carefully designed diffusion measurements can be made to ascertain quantitatively the effects of hydrogen bonding on diffusion. In this paper, we present limiting mutual diffusion coefficients of polar aromatic solutes in acetone and report calculated interaction energies⁴⁴ for 1:1 solute–acetone complexes. The purpose of this work is to demonstrate, with the help of the present data and previous results, an understanding of the molecular dynamics of associated molecules in

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terms of strong intermolecular interactions, an area which has been underdeveloped.

II. EXPERIMENT

Measurements of the mutual diffusion coefficients at trace concentration were made by using the chromatographic peak-broadening method, known also as the Taylor dispersion technique. The apparatus was similar in design to that reported elsewhere.⁶ In this study, however, the solvent was delivered by a Bio-Rad HPLC pump (Model 1350) with a flow rate precision of $\pm 0.1\%$, and the solute dispersion peak was detected with a Dynamax differential refractometer (Model RI-1). The experimental procedures have been described previously.⁶ Briefly, a small 20–50 μL sample of a dilute solution was injected into a stream of solvent in a capillary diffusion tube. 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., which was coiled in a circle with a diameter of about 40 cm and immersed in a water bath controlled to within ± 0.02 K. To ensure laminar flow, the solvent flow rate was adjusted so that the constant volume flow was between 0.1 and 0.2 mL min^{-1} . At the end of the diffusion tube, the solute dispersion peak was detected by the differential refractometer and recorded with a chart recorder. In this work, the solute mesitylene (98%, Riedel-de Haen) was purified by fractional distillation; phenol (99.5%, E. Merck), *p*-cresol (99%+, Fluka), *p*-chlorophenol (99.5%+, BDH), 1-naphthol (99%+, Aldrich), 2-naphthol (99%, Aldrich), biphenyl-2-ol (99%+, E. Merck), aniline (99.5%+, Aldrich), *p*-toluidine (99.9%, Aldrich), *p*-chloroaniline (99%+, Fluka), 4-chloro-2-methylaniline (99%, Aldrich), 1-naphthylamine (99%+, E. Merck), 2-biphenylamine (98%+, E. Merck), acetophenone (99%, Aldrich), propiophenone (99%+, E. Merck), 2-naphthalenethiol (99%, E. Merck), anisole (99%+, E. Merck), *p*-methylanisole (99%+, E. Merck), *p*-chloroanisole (98%+, Fluka), and

2-methoxynaphthalene (99%, Aldrich) were used as received. The solvent acetone (99.9%+, Aldrich) was filtered before use with 20 μm stainless steel HPLC solvent filter. All data were recorded at 298.15 ± 0.02 K. Temperature was measured using a Beckmann thermometer calibrated with a certified thermometer (Baird and Tatlock, No. GDZ27736). At least three measurements were made to obtain a diffusion coefficient, the average error being normally $\pm 1\%$.

Molecular interaction energies of 1:1 solute–acetone complexes were determined by *ab initio* molecular orbital calculations, using the GAUSSIAN94 system of program. Geometry optimizations for molecules as well as complexes were carried out at the HF/6-31G(*d*) level of theory. In constructing a complex from molecules, the hydrogen-bond length $r_{\text{H}\cdots\text{O}}$ (where H is contributed from solute and O from acetone) was given an initial value of 2.5 Å, and the bond angle $\alpha_{\text{XH}\cdots\text{O}}$ (where X represents O in phenols, N in aromatic amines, S in 2-naphthalenethiol, and C in other solutes) was initially assigned as 180°, followed by full geometry optimization. All optimized structures were confirmed to be minimum on the potential-energy surface by frequency calculation. These structures will be reported elsewhere.⁴⁵ Furthermore, electron correlation was incorporated via single point energy calculations at the second order Møller–Plesset perturbation theory (MP2) with the triply split valence 6-311G(*d,p*) basis. For systems involving weak interactions of individual entities, it has been shown⁴⁶ that the basis set superposition error (BSSE) may be significant. Thus, in the calculation of the interaction energy, ΔE , the BSSE is corrected by the full counterpoise correction as follows:

$$\Delta E = E(AB) - [E(A)_{A(B)} + E(B)_{(A)B}] + \Delta ZVPE, \quad (2)$$

where $E(AB)$ is the MP2/6-311G(*d,p*) energy of the complex; $E(A)_{A(B)}$ and $E(B)_{(A)B}$ represent the electronic energies at the MP2/6-311G(*d,p*) level of theory (with the full basis set contributed from both *A* and *B*), using the

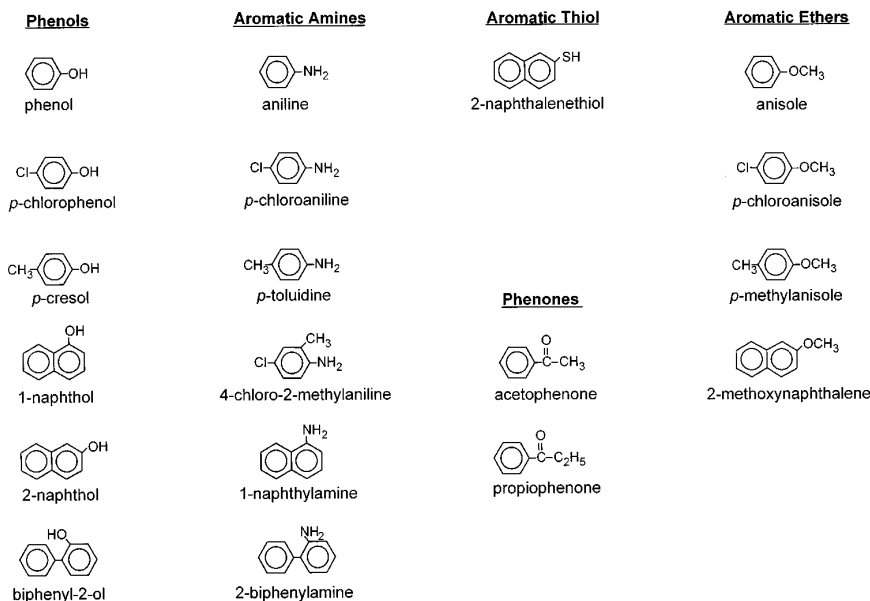
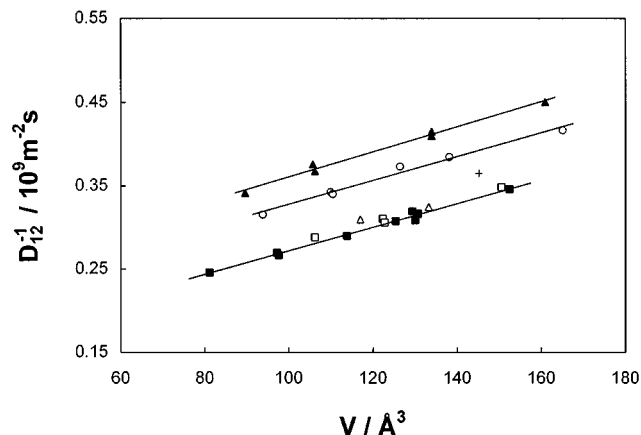


TABLE I. Limiting mutual diffusion coefficients of pseudoplanar solutes in acetone at 298.2 K.

	VDW vol/ \AA^3 ^a	$D_{12}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$D'_{12}/10^{-9} \text{ m}^2 \text{ s}^{-1d}$
<u>Nonassociated solutes</u>			
Benzene	81.1	4.07 ± 0.04^b	
Chlorobenzene	97.2	3.71 ± 0.03^b	
Toluene	97.6	3.75 ± 0.03^b	
Ethylbenzene	113.8	3.45 ± 0.02^b	
Naphthalene	125.4	3.25 ± 0.03^b	
1,2,4-Trichlorobenzene	129.3	3.13 ± 0.03^b	
Propylbenzene	130.0	3.24 ± 0.03^b	
Mesitylene	130.7	3.16 ± 0.03	
Biphenyl	152.4	2.89 ± 0.03^b	
<u>Phenols</u>			
Phenol	89.6	2.93 ± 0.03 (2.97 ± 0.03^c)	2.90
<i>p</i> -Chlorophenol	105.7	2.66 ± 0.03	2.72
<i>p</i> -Cresol	106.2	2.72 ± 0.03 (2.74 ± 0.03^c)	2.71
1-Naphthol	133.9	2.44 ± 0.02	2.45
2-Naphthol	133.9	2.41 ± 0.02	2.45
Biphenyl-2-ol	160.9	2.22 ± 0.02	2.24
<u>Aromatic amines</u>			
Aniline	93.8	3.17 ± 0.04^c	3.27
<i>p</i> -Chloroaniline	109.9	2.92 ± 0.03^c	3.05
<i>p</i> -Toluidine	110.4	2.94 ± 0.03^c	3.04
4-Chloro-2-methylaniline	126.4	2.68 ± 0.03	2.84
1-Naphthylamine	138.1	2.60 ± 0.02	2.71
2-Biphenylamine	165.1	2.40 ± 0.02	2.46
<u>Aromatic thiol</u>			
2-Naphthalenethiol	145.1	2.74 ± 0.02	2.67
<u>Phenones</u>			
Acetophenone	117.0	3.23 ± 0.03	
Propiophenone	133.2	3.08 ± 0.04	
<u>Aromatic ethers</u>			
Anisole	106.2	3.47 ± 0.03	
<i>p</i> -Chloroanisole	122.3	3.22 ± 0.04	
<i>p</i> -Methylanisole	122.7	3.27 ± 0.03	
2-Methoxynaphthalene	150.5	2.87 ± 0.03	

^aThe values are averages from Refs. 47–50.^bFrom Ref. 6.^cFrom Ref. 43.^dCalculated values from Eqs. (3) and (4).FIG. 1. Variation of $1/D_{12}$ with molecular volume of solutes diffusing in acetone at 298.2 K: (■) nonassociated solutes, (□) aromatic ethers, (△) phenones, (+) 2-naphthalenethiol, (○) aromatic amines, and (▲) phenols.TABLE II. Solvation numbers (n) for polar solutes in acetone.

	n
<u>Phenols</u>	
Phenol	1.0 ± 0.1
<i>p</i> -Chlorophenol	1.1 ± 0.1
<i>p</i> -Cresol	1.0 ± 0.1
1-Naphthol	1.0 ± 0.1
2-Naphthol	1.1 ± 0.1
Biphenol-2-ol	1.1 ± 0.1
<u>Aromatic amines</u>	
Aniline	0.6 ± 0.1
<i>p</i> -Chloroaniline	0.6 ± 0.1
<i>p</i> -Toluidine	0.6 ± 0.1
4-Chloro-2-methylaniline	0.7 ± 0.1
1-Naphthylamine	0.7 ± 0.1
2-Biphenylamine	0.6 ± 0.1
<u>Aromatic thiol</u>	
2-Naphthalenethiol	0.3 ± 0.1

HF/6-31G(*d*) geometry of *A* and *B*, respectively, in the complex *AB*; $\Delta ZVPE$ is the zero-point vibrational energy correction calculated using HF/6-31G(*d*) frequencies, scaled by 0.9.

III. RESULTS AND DISCUSSION

The structures of solutes containing one polar group in this work are shown in the section above. All solutes studied are pseudoplanar in shape. The measured diffusion coefficients are summarized in Table I. The uncertainty listed is the average absolute error, and the reproducibility of data here is consistent with those reported in our previous works^{6,43} using the same technique. Table I also includes values of the VDW volume of the solute monomers, which are calculated from group increments given in the literature.^{47–50}

For the nonassociated pseudoplanar solutes, a linear relationship exists between $1/D_{12}$ and *V*. The linear regression line is shown in Fig. 1. Also presented in this figure are values for other solutes given in Table I. All $1/D_{12}$ data for phenols, aromatic amines and 2-naphthalenethiol show positive deviation from the “nonassociated” line in Fig. 1, indicating that the diffusivities of the solutes are retarded by solute–solvent interactions. The deviations vary from about 9% in the case of 2-naphthalenethiol to ~34% for *p*-chlorophenol. 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. It should also be noted that aniline has been known not even self associated in nonpolar solvent.⁶ Figure 1 shows that phenones and aromatic ethers behave practically as nonassociated solutes. The results are not unexpected as these molecules are incapable of forming hydrogen bonds with the solvent. It is interesting to note that linear relationship between $1/D_{12}$ and *V* is also found for phenols as well as amines. The regression lines (all with correlation coefficient >0.992) are displayed also in Fig. 1. Remarkably, the slopes for all straight lines in the figure are about the same. This indicates that the effects of hydrogen bonding on diffusion are due mainly to the type of polar group attached. For solutes containing the same polar group, however, the effects are approximately equal. To illustrate our point, one may consider 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 of a diffusing complex can actually be evaluated from the diffusion coefficient of the polar solute. This is done by determining the equivalent volume from the $1/D_{12}$ vs. *V* regression line for the nonassociated solutes, using the diffusion data of the polar solute. The calculated volume of complex in excess of the monomeric solute volume is the average volume of solvent molecules associated with the solute. It follows that the average number of acetone molecules associated with a solute can be determined from this excess volume and the VDW volume of acetone. The solvation numbers thus calculated for phenols, aromatic amines and 2-naphthalenethiol, together with their estimated uncertainties, are given in Table II. From this table, it can be seen that

TABLE III. Interaction energies (ΔE) of solute–acetone complexes.

Solute	$\Delta E/\text{kJ mol}^{-1}$
Phenol	–22.8
<i>p</i> -Cresol	–22.4
Aniline	–14.0
<i>p</i> -Toluidine	–13.7
2-Naphthalenethiol	–13.1
Anisole	–7.8
<i>p</i> -Methylanisole	–7.7
Acetophenone	–6.8
Ethylbenzene	–6.3
Toluene	–5.7
Benzene	–4.8

all phenols on the average diffuse together with about one acetone molecule, all aromatic amines with ~0.6, and 2-naphthalenethiol with ~0.3. This indicates that the strength of polar group associated with acetone through hydrogen bonding is greater in the order $-\text{OH} > -\text{NH}_2 > -\text{SH}$, and that for solutes with the same polar group the strength is relatively independent of the size and mass of the molecule.

One feature of the results in Table II is that all solvation numbers are either approximately equal to or less than one. This is not surprising in the case of acetone as solvent as only oxygen in acetone is available for hydrogen bonding. It should be noted that hydrogen bonds between solute and solvent molecules are continuously breaking and forming. On the average, the number of solvent molecules associated with a solute molecule may be less than one, depending on the strength of hydrogen bonding.

Ab initio molecular orbital calculations have been carried out to obtain the interaction energies of some representative 1:1 solute–acetone complexes. The results are given in Table III. It should be pointed out that ΔE calculated for acetone–acetone dimer is -6.4 kJ mol^{-1} . This value is about the same as those calculated for the nonassociated compounds as well as the aromatic ethers and phenone in Table III. Nonetheless, ΔE values for the phenols, aromatic amines, and aromatic thiol show significant deviations from that of the acetone–acetone dimer, suggesting that strong intermolecular interactions may occur between these solutes and acetone in solution. In fact, the values of ΔE appear to be consistent with our diffusion results of hydrogen-bond strength, i.e., $-\text{OH} > -\text{NH}_2 > -\text{SH}$. It is interesting to examine the variation of ΔD_{12}^{-1} , the deviation of a polar solute’s $1/D_{12}$ value from the nonassociated line in Fig. 1 at the same monomeric solute volume, with the interaction energy. Figure 2 shows that an approximately linear relationship exists between ΔD_{12}^{-1} and ΔE . The data indicate that the effect of molecular association on diffusion in dilute solutions is proportional to the interaction energy.

The implications of our data on the applicability of the RHS theory to the diffusion of associated molecules are noteworthy. As a polar solute acts like a complex in diffusion, the RHS theory which has been successful for the interpretation of the diffusion of nonassociated molecules in condensed phase should also be applicable for describing the

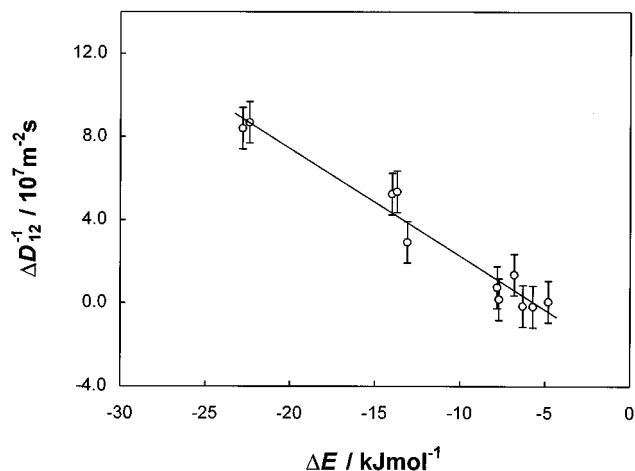


FIG. 2. Correlation between ΔD_{12}^{-1} and solute-acetone interaction energy.

diffusion behavior of polar solutes, provided that the complex size [i.e., σ_1 in Eq. (1)] is known. More importantly, the present data also suggest that the RHS theory as represented by Eq. (1) may be alternatively modified to predict limiting mutual diffusion coefficients of associated molecules as follows:

$$1/D'_{12} = 1/D_{12}^{\text{RHS}} + \Delta D_{12}^{-1}, \quad (3)$$

where D'_{12} refers to the limiting mutual diffusion coefficient of an associated solute, D_{12}^{RHS} is the diffusivity of the similar nonassociated solute which may be represented by Eq. (1), and ΔD_{12}^{-1} is a function of interaction energy at a given temperature and solvent. For acetone as solvent at 298.2 K, ΔD_{12}^{-1} can be expressed by

$$\Delta D_{12}^{-1}/10^7 \text{ m}^{-2} \text{ s} = -0.5172 \times \Delta E/\text{kJ mol}^{-1} - 2.915. \quad (4)$$

The correlation coefficient of Eq. (4) is 0.977, and this equation fits all ΔD_{12}^{-1} data to an average error of $\pm 0.61 \times 10^7 \text{ m}^{-2} \text{ s}$. The result of the regression is quite reasonable in consideration of the experimental errors of the diffusion data. When the average ΔE value ($-22.6 \text{ kJ mol}^{-1}$) of phenol and *p*-cresol is taken as the value for all phenols and $-13.85 \text{ kJ mol}^{-1}$ (the average ΔE value of aniline and *p*-toluidine) for all aromatic amines, all absolute values of D'_{12} predicted by Eq. (3) using the nonassociated line for D_{12}^{RHS} and Eq. (4) for ΔD_{12}^{-1} agree with the experimental values of all associated solutes in this study to within 5.9%, the average error being only 2.5%. The calculated values are shown also in Table I.

IV. CONCLUSIONS

Carefully designed measurements of diffusion coefficients can provide significant information on the transport behavior of associated molecules in dilute solutions. In this study, it is found that the effects of solute-solvent association on diffusion are approximately equal for solutes containing the same polar group. The effects are nonetheless different for different functional groups, with $-\text{OH} >$

$-\text{NH}_2 > -\text{SH}$ in acetone at 298.2 K. By comparing the diffusion coefficients of the associated and nonassociated solutes, solvation numbers which indicate the degree of molecular association have been determined for various solutes. We have also demonstrated here that the diffusion of associated molecules can be understood in terms of the rough-hard-sphere theory and the solute-solvent interaction energy.

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