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Steric effects on diffusion of associated molecules in acetone

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The effects due to steric hindrance on solute–solvent interactions and on diffusion of associated molecules were found by comparing the diffusion coefficients of different aromatic isomers in acetone at 298.2 K; there exists a correlation between the isomeric effects of intermolecular association on diffusion and the molecular scales of overall hydrogen-bond acidity of the isomers studied.

Although several studies of the mutual diffusion of associated molecules have been reported,[1–8] our understanding of the diffusion behaviour of molecules capable of strong solute–solvent interactions is still rudimentary. Molecules of this type, however, are of practical importance as they occur commonly in nature and in many chemical systems. Here, we present newly measured mutual diffusion coefficients of aromatic compounds at trace concentration (D_{12}) in acetone at 298.15 ± 0.02 K, and the steric effects on mutual diffusion of molecules with solute–solvent H-bonding are reported. Diffusivities were measured by Taylor's dispersion method; the apparatus and procedures used were similar to those described before.[1,2] In this study, however, the solvent was delivered by an Agilent HPLC pump (Model 1100) with a flow rate precision of ±0.5%. The solvent acetone (99.9%+) was degassed by ultrasonic bath and then filtered before use with a 20 μm stainless-steel solvent filter. The solute 1,3,5-trimethylbenzene (98%) was purified by fractional distillation; all other solutes were 99% or above in purity and were used as received. To test our new equipment, the data for benzene and 1,2,4-trichlorobenzene were measured again; our present $D_{12}/10^{-9}$ m^2 s^{-1} values of 4.08 ± 0.04 and 3.09 ± 0.04, respectively, agree well with the previous data[9] within experimental error.

The measured D_{12} data are summarized in Table 1. Also shown in the table are values of the van der Waals (VDW) volume of the solute monomers, which are calculated from group increments.[10–13] For solutes incapable of forming H-bonds with the solvent acetone, there appears to be very little effect of shape on diffusivities for the different isomers with the same molecular size (see data of the non-H-bonded solutes in Table 1). Similar results of the insensitivity of solute shape on diffusion in acetone have also been reported,[9,14] which was attributed to the small molecular size of acetone.[9] By comparing the D_{12} data of the 2- and 3-methylphenols, it can be seen that there is a small difference of about 2.6%. The larger value of 2-methylphenol is probably due to the steric repulsion effect provided by its –CH$_3$ in the *ortho* position, which hinders the attachment of acetone to the solute's –OH *via* H-bonding. A lower degree of solute–solvent association is known to result in a smaller overall complex and thus a faster diffusion rate. In fact, the degree of solute–solvent association can be measured[1] by $\Delta D_{12}{}^{-1}$ as given by the following expression:

$$\Delta D_{12}{}^{-1} = 1/D_{12} - 1/D_{12}{}^{\mathrm{N}} \qquad (1)$$

where $D_{12}{}^{\mathrm{N}}$ is the diffusion coefficient of the non-associated solute. For non-associated aromatic compounds diffusing in acetone, it has been shown[2] that a linear relationship exists between $1/D_{12}{}^{\mathrm{N}}$ and the VDW volume of the solutes. The linear 'non-associated' line is displayed in Fig. 1; it can be represented by the following equation:

$$(D_{12}{}^{\mathrm{N}})^{-1}/10^9\,\mathrm{m}^{-2}\mathrm{s} = 1.41(\pm 0.05) \times 10^{-3} V/\text{Å}^3 + 0.131(\pm 0.006) \qquad (2)$$

where V is the VDW volume of the non-associated solutes. The standard deviation of the fit is 0.0034, and the correlation coefficient is 0.989. Eqn. (2) fits all data within 1.9%.[2] Also shown in the figure are the $1/D_{12}$ data for the associated solutes. All these data deviate positively from the 'non-associated' line since the diffusivities are retarded by the volume increase due to H-bonding of the solutes with acetone. The $\Delta D_{12}{}^{-1}$ values calculated from the deviations of $1/D_{12}$ from the 'non-associated' line are presented in Table 1.

The steric repulsion effect can be seen more significantly in the disubstituted phenols. There is a difference of about 9% in D_{12} between 2,6-dimethylphenol and 4-chloro-3-methylphenol. The data clearly indicate that 2,6-dimethylphenol with two methyl groups next to the hydroxy group diffuses faster than those with only one (*i.e.* 2,5-dimethylphenol and 2-chloro-

Table 1 Limiting mutual diffusion coefficients (D_{12}) of aromatic compounds in acetone at 298.2 K

		V^a/Å^3	10^9 D_{12}/m^2 s^{-1}	10^{-8} ΔD_{12}^{-1} /m^{-2} s	$\Sigma\alpha^{\mathrm{H}c}$	10^9 D_{12}^{cal} /m^2 s^{-1}
Non-H-bonded solutes	2-Nitrotoluene	120.6	3.11 ± 0.03			
	3-Nitrotoluene	120.6	3.14 ± 0.03			
	1,2,4-Trimethylbenzene	130.7	3.16 ± 0.04			
	1,3,5-Trimethylbenzene	130.7	3.16 ± 0.03^b			
	2-Nitro-*m*-xylene	137.2	2.91 ± 0.02			
	4-Nitro-*o*-xylene	137.2	2.94 ± 0.03			
Mono-H-bonded solutes	2-Methylphenol	106.2	2.78 ± 0.02	0.790	0.52	2.78
	3-Methylphenol	106.2	2.71 ± 0.03	0.883	0.57	2.72
	2,6-Dimethylphenol	122.7	2.75 ± 0.03	0.596	0.39	2.75
	2,5-Dimethylphenol	122.7	2.61 ± 0.02	0.791	0.54	2.59
	2-Chloro-5-methylphenol	122.2	2.59 ± 0.03			
	4-Chloro-3-methylphenol	122.2	2.52 ± 0.02	0.935	0.65	2.49
Di-H-bonded solutes	1,2-Dihydroxybenzene	98.1	2.50 ± 0.02	1.31	0.85	2.51
	1,3-Dihydroxybenzene	98.1	2.27 ± 0.02	1.71	1.10	2.29
	1,4-Dihydroxybenzene	98.1	2.26 ± 0.02	1.73	1.16	2.24

^{a} Van der Waals volumes are averages from refs. 10–13. ^{b} From ref. 2. ^{c} From ref. 16.

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5-methylphenol), which in turn is faster than 4-chloro-3-methylphenol without an *ortho* substituent. It should be pointed out that 2,5-dimethylphenol and 2-chloro-5-methylphenol are of about the same shape and size, and that Table 1 shows their diffusion coefficients are approximately equal, indicating that a –Cl can be considered as equivalent to a $-CH_3$ in the diffusion of the disubstituted phenols. Similar results of the resemblance between a –Cl and a $-CH_3$ in diffusion have already been discussed.[6,15] Table 1 also shows that ΔD_{12}^{-1} drops about 15% from 4-chloro-3-methylphenol to 2,5-dimethylphenol. The value for 2,6-dimethylphenol is significantly lower by 36% as compared to that of 4-chloro-3-methylphenol. Since the effects of shape and mass as well as the electronic effect are relatively unimportant in the above phenols studied, it is clear that the differences in D_{12} and ΔD_{12}^{-1} are due mainly to the steric repulsions that weaken the solute–solvent interactions. The effect is greater for 2,6-dimethylphenol which has two adjacent groups.

The values of ΔD_{12}^{-1} for the mono-H-bonded phenols without a $-CH_3$ or –Cl substituent in the *ortho* position are quite close ($\sim 0.91 \pm 0.02 \times 10^8$ m^{-2} s), regardless of the different sizes of the solutes. The result is consistent with our earlier findings[2,6] that the degrees of association or ΔD_{12}^{-1} values are approximately the same for all mono-H-bonded aromatic solutes containing the same polar group (*e.g.* –OH) and without an *ortho* substitution (steric repulsion), regardless of the sizes. It is of interest to note that the ΔD_{12}^{-1} values are also nearly equal for 2-methylphenol (0.790×10^8 m^{-2} s) and the larger 2,5-dimethylphenol (0.791×10^8 m^{-2} s), even though their values are different from those of the solutes without *ortho* hindrance. This is not unexpected, however, as the steric hindrance is provided by the same *ortho* substituent in both molecules. The steric repulsion due to the presence of an adjacent methyl group lowers the ΔD_{12}^{-1} values by an average $0.12(\pm 0.02) \times 10^8$ m^{-2} s or 13% in the degree of solute–acetone association.

Comparisons of data between the di-H-bonded solutes show that the diffusivity of 1,2-dihydroxybenzene is about 10% higher than those of the other dihydroxybenzenes without *ortho* substitution. From the $\Delta D_{12}^{-1}/10^8$ m^{-2} s values, it appears that the degrees of association of 1,3- and 1,4-dihydroxybenzenes are about the same and additive (*i.e.* they are contributed from each independent –OH in the molecule). For example, the value of 1.71 for 1,3-dihydroxybenzene is about twice that of 0.883 for 3-methylphenol. This is reasonable since all these molecules are quite free of steric hindrance to the incoming acetone. Nonetheless, there is a decrease of 28% in ΔD_{12}^{-1} for 1,2-dihydroxybenzene, which can probably be attributed partly to the intramolecular H-bonding and partly to the steric hindrance provided by the adjacent hydroxy groups together with their attachments.

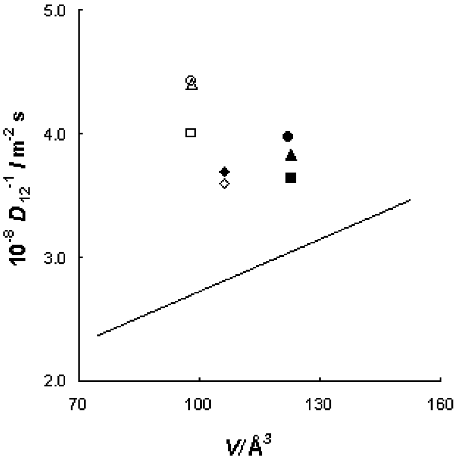

Fig. 1 Deviation of $1/D_{12}$ from the non-associated line of acetone at 298.2 K: (○) 1,4-dihydroxybenzene, (Δ) 1,3-dihydroxybenzene, (□) 1,2-dihydroxybenzene, (◆) 3-methylphenol, (◇) 2-methylphenol, (●) 4-chloro-3-methylphenol, (▲) 2,5-dimethylphenol, and (■) 2,6-dimethylphenol.

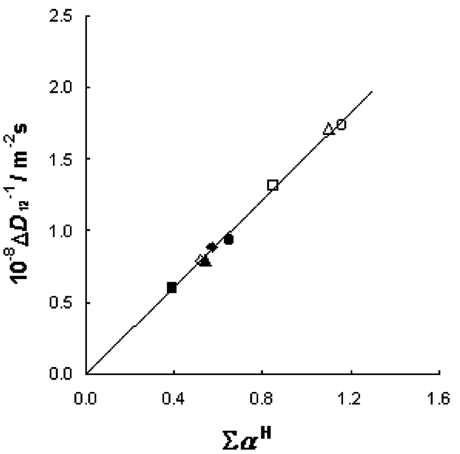

Fig. 2 Variation of ΔD_{12}^{-1} with overall hydrogen-bond acidity of solutes in acetone at 298.2 K (see Fig. 1 for symbols used).

Recently, we have successfully correlated ΔD_{12}^{-1} of solutes containing no *ortho* substitution in acetone with the effective solute H-bond acidity scales.[1] These overall acidities ($\Sigma\alpha^H$) of solutes were derived from complexation constants, and should have taken the steric repulsion effect into account. The degree of solute–solvent association should be dependent only on the product of $\Sigma\alpha^H$ of solutes and the overall basicity ($\Sigma\beta^H$) of acetone, since acetone can act only as a H-bond-acceptor. As $\Sigma\beta^H$ of acetone can be taken as constant in the system studied, ΔD_{12}^{-1} is therefore expected to be proportional only to $\Sigma\alpha^H$ of the solutes; the values of those available in the literature[16] are listed in Table 1. Fig. 2 shows that a linear relationship was indeed obtained when ΔD_{12}^{-1} was plotted against $\Sigma\alpha^H$. All values of ΔD_{12}^{-1} were fitted very well by

$$\Delta D_{12}^{-1}/10^8 \text{ m}^{-2} \text{ s} = 1.52\ \Sigma\alpha^H \qquad (3)$$

The standard deviation of the fit is 3.09×10^{-2}. When eqn. (2) and eqn. (3) are substituted into eqn. (1), the values of D_{12} calculated from eqn. (1) are given also in Table 1.

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