Hydrogen Bonding with Aromatic Rings

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Thermodynamic effects of hydrogen bonding are important in determining the phase behavior in polar fluids. While efforts to understand ''strong'' donor and ''strong'' acceptor combinations (H-bonds involving a formation energy more negative than −20 kJ/mol such as alkanol-alkanol H-bonding have been substantial, weak H-bonds (involving double bonds or aromatic rings as proton acceptors) have largely been ignored. Using FTIR spectroscopy H-bonding between alcohol donor and aromatic ring-containing acceptor molecules was studied including l-hexanol and cyclohexanol at low concentrations where self-association is negligible (strong donors). H-bonding ''weak'' acceptors studied include toluene and m-xylene. Clear spectroscopic evidence existed for the formation of H-bonds between the alcohol and aromatic molecules, which are much weaker than conventional ''strong donor''–''strong acceptor'' H-bonds. Using quantitative FTIR measurements, the percentage of H-bonded alcohol molecules over a range of aromatic concentrations was determined. Ab initio calculations also showed that alcohol−aromatic H-bonds are much weaker than alcohol−alcohol H-bonds. This H-bonding, though weak, will contribute significantly to the chemical potential of the molecules.

Introduction

Hydrogen bonds (H-bonds) are traditionally defined as occurring between a donor hydrogen atom and an electronegative acceptor atom with lone electron pairs (Pimentel and McClellan, 1960; Panayiotou and Sanchez, 1991; Veytsman, 1990). Examples of such systems are the self-H-bonding of water and alcohol molecules (Tonge et al., 1996), of amino acids (Noguchi et al., 1999), and the intramolecular H-bonding present in glycol ethers (Brinkley and Gupta, 1998). However, H-bonds are largely electrostatic in nature, and therefore other suitable sources of electrons could also act as an acceptor group. One such source of electrons is the hybridized π-bonds of an aromatic ring.

An extensive amount of work has been put into simulating aromatic interactions with H-bond donors. Cheny and coworkers (1988) used *ab initio* calculations to find the binding energies of hydrogen fluoride, hydrogen chloride, water, hydrogen sulfide, and ammonia paired with benzene. Bredas and Street (1988) comfirmed that hydrogen fluoride H-bonds to the aromatic ring using *ab initio* calculations performed on various conformations of the two molecules. The following year, Bredas and Street (1989) used similar techniques to demonstrate H-bonding in pyrene/water and benzene/formic acid pairs. More recently, Rozas and coworkers (1997) compared the relative H-bonding energies of hydrogen fluoride with acetylene, ethylene, benzene, and other compounds containing double and triple carbon−carbon bonds. Samanta and coworkers (1998) used molecular orbital calculations to study the effect of heteroatomic aromatic rings by simulating pyridine dimers with water and ammonia. Despite the amount of *ab initio* work in this area, however, very few attempts have been made to verify the energetics of aromatic H-bonding interactions through experiments. Due to the fact that the energy of this interaction is much lower than the ''classic'' H-bond (approximately −10 kJ/mol compared to −30 kJ/mol), the IR and NMR shifts used to identify H-bonded complexes are rather small, as shown in Figure 1.

Binary molecular interactions are well probed using activity coefficients at infinite dilution (γ^{∞}). At infinite dilution, a solute molecule is only affected by the interaction with the surrounding solvent molecules. Therefore, infinite-dilution activity coefficients give an indication of the relative intermolecular interactions between a pair of molecules. For example, an ethanol molecule surrounded by other ethanol molecules is considered to have unity activity coefficient,

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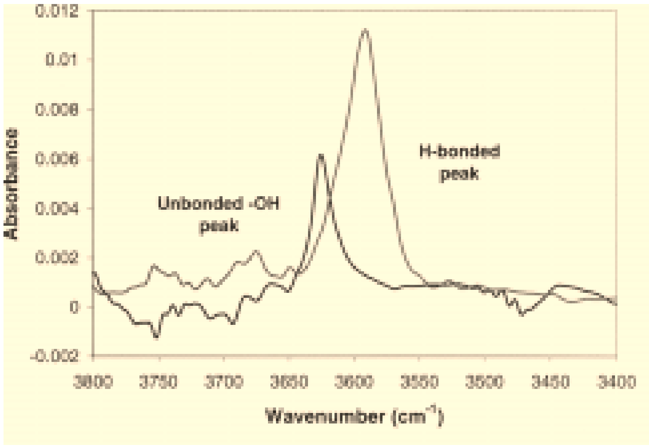

Figure 1. Comparison of the OH stretching FTIR peaks due to non-H-bonded (*n*-hexane) and H-bonded (in toluene) *l*-hexanol.

while an ethanol molecule placed in a noninteracting solvent would yield a γ^{∞} greater than one. If an ethanol molecule were to be placed in a solvent with which it had a stronger interaction than ethanol, the γ^{∞} would be less than one. For ethanol, γ^{∞} in hexane, benzene, and toluene solvents are reported by Thomas et al. (1982) and Tiegs et al. (1986) at varying temperatures (Figure 2). A very interesting trend is observed: γ^{∞} is much lower in toluene or benzene than in hexane. While γ^{∞} does not indicate that ethanol associates more strongly with benzene or toluene than it does with itself, it does appear to indicate a significantly greater affinity for benzene and toluene compared to hexane. This could be explained by the occurrence of H-bonding (attractive force) between the ethanol molecule and the benzene ring. As the temperature increases, the difference in γ^{∞} decreases, due to breakage of the H-bonds. At higher temperatures, toluene and benzene behave more like hexane due to decreased H-bonding of ethanol with the aromatic rings, as a result of the increased kinetic energy of the molecules.

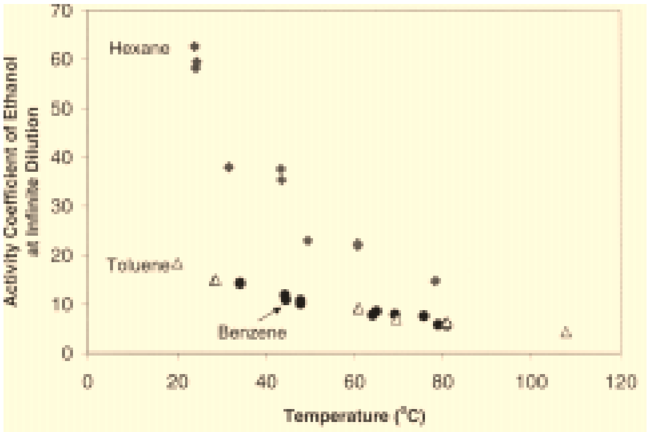

Figure 2. Activity coefficient of ethanol at infinite dilution in hexane, toluene, and benzene solvents (Data from Thomas et al., 1982, and Tiegs et al., 1986.)

In this work, we examine the H-bonding between alcohols and aromatic molecules using FTIR spectroscopy. FTIR spectra are obtained for mixtures containing 1-hexanol/toluene, 1-hexanol/*m*-xylene, and cyclohexanol/toluene. Non-H-bonded alcohol is dissolved in an alkane solvent, then increasing amounts of toluene or *m*-xylene are added to form H-bonds. The extent of H-bonding in each pair is obtained from spectral analysis; these results are then compared to alcohol/alcohol H-bonding. *Ab initio* calculations are also carried out to obtain further understanding.

Experimental Studies

Apparatus and material

The FTIR apparatus is the same as described in our previous work (Gupta and Brinkley, 1998) on alcohol self-association. The only addition to this apparatus was a cooling coil before the heater/controller so experiments could be performed at subambient temperatures. The cooling coil was submerged in an antifreeze solution that was cooled by an immersion chiller (Lauda, model IC-30). All the chemicals, toluene (Fisher, No. T324-4), *m*-xylene (Aldrich, No. 29,632-5), *l*-hexanol (Aldrich, No. 12079-0025), cyclohexanol (Aldrich, No. 10,589-9), *n*-hexane (Fisher, No. H302-4), and methylcyclohexane (Aldrich, No. M3,788-9) were dried overnight at room temperature with 4-Å molecular sieves (Fisher, No. M514-500) to remove any trace amounts of water prior to use. Background moisture was removed by purging the compartment with nitrogen (BOC, grade 5.0) for one hour. The FTIR cell and all tubing are insulated to aid in temperature control (within 0.1°C).

In a typical experiment, background spectrum was recorded for the alkane/aromatic mixture of the desired composition. Then alcohol was injected in the system, and the spectrum recorded. The spectrum was an average of 100 scans to improve the signal-to-noise ratio. Each experiment was repeated four times and an average of the results was taken. The experimental error in the peak area count was expected to be about 5%.

Spectral Analysis

At low alcohol concentrations (mol fraction, $x_{\text{alcohol}} < 0.0005$) alcohol is unable to self-associate (Gupta and Brinkley, 1998), and only one OH peak, corresponding to free (that is, non-H-bonded) alcohol molecules is formed at 3,630 cm^{-1}. If a sufficient amount of toluene or other aromatic-containing compound is added to the mixture, a second peak representing the H-bonded OH vibration will form at 3,590 cm^{-1} (Figure 3). Due to the weak nature of the alcohol–aromatic hydrogen bond, the IR frequency shift is small (approximately 40 cm^{-1}). Rather than use a peak separation technique, we chose to take advantage of the fact that the free and H-bonded alcohol molecules have different extinction coefficients, and the total area (from 3,550 cm^{-1} to 3,675 cm^{-1}) of the two peaks grows as more H-bonds are formed. According to Beer's law the total area, A_{total}, is given as

$$A_{\text{total}} = l\epsilon_{\text{free}}C_{\text{free}} + l\epsilon_{\text{H-bonded}}C_{\text{H-bonded}}, \qquad (1)$$

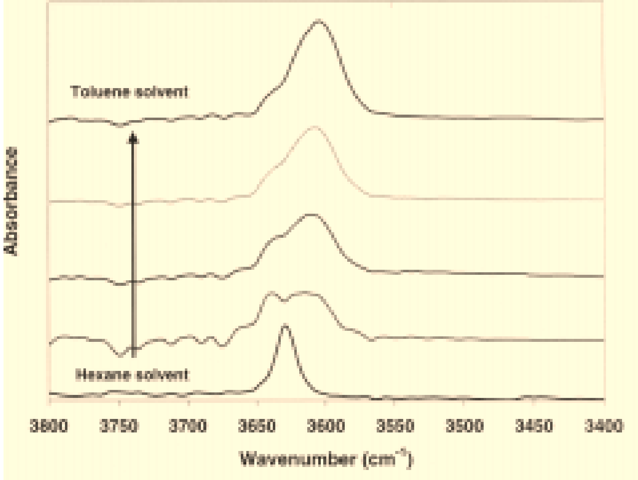

Figure 3. Effect of toluene concentration on the FTIR spectra of 1-hexanol/toluene/*n*-hexane mixtures, at 35°C.

where ϵ_{free} is the extinction coefficient of the non-H-bonded alcohol peak; $\epsilon_{\text{H-bonded}}$ is the extinction coefficient of the H-bonded alcohol peak; C_{free} is the concentration of the free, non-H-bonded alcohol molecules; $C_{\text{H-bonded}}$ $(= C_{\text{total}} - C_{\text{free}})$ is the concentration of the H-bonded alcohol; C_{total} is the total alcohol concentration; l is the path length of the cell; and A_{total} refers to the total area of the two peaks.

The values of extinction coefficient ϵ_{free} are obtained from the spectra of alkanols in pure alkanes, when H-bonding is not present. Similarly, the values of extinction coefficient $\epsilon_{\text{H-bonded}}$ are obtained from the spectra of alkanol in pure aromatic solvents at a low temperature (18°C), where complete H-bonding is present. These values are listed in Table 1.

In these experiments, the mixtures were prepared by volumetric addition of pure components. Using pure-component densities, mol fractions were calculated. Now, calculating the molar concentration of the alcohol in the mixture, C_{total}, and molar density of the mixture, ρ_{mixture}, assuming ideal volume of mixing:

$$\frac{1}{\rho_{\text{mixture}}} = \frac{x_{\text{alkane}}}{\rho_{\text{alkane}}} + \frac{x_{\text{aromatic}}}{\rho_{\text{aromatic}}} + \frac{x_{\text{alcohol}}}{\rho_{\text{alcohol}}}. \tag{2}$$

Table 1. Extinction Coefficients for Free and Bonded Peaks

Alcohol	Solvent	$\rho_{\text{solvent}} l \epsilon_{\text{free}}$	$\rho_{\text{solvent}} l \epsilon_{\text{H-bonded}}$
l-Hexanol	*n*-Hexane	1,502	—
l-Hexanol	Toluene	—	5,313
l-Hexanol	*m*-Xylene	—	4,773
Cyclohexanol	Methylcyclohexane	1,170	—
Cyclohexanol	Toluene	—	4,314

Note: ρ_{solvent} is the molar density of solvent; the unit of $\rho_{\text{solvent}} l \epsilon_{\text{free}}$ is absorbance/cm.

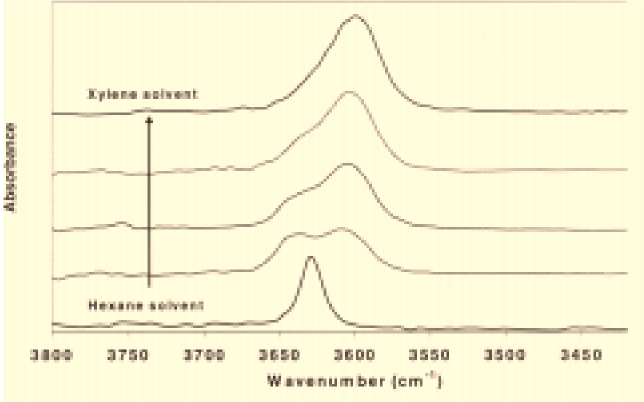

Figure 4. Effect of *m*-xylene concentration on the FTIR spectra of 1-hexanol/*m*-xylene/*n*-hexane mixtures, at 35°C.

The contribution of the alcohol, $x_{\text{alcohol}}/\rho_{\text{alcohol}}$, is negligible due to the very small amount of alcohol involved. It is safe to assume the ideal volume of mixing, due to the fact that the chosen alkanes and aromatics are relatively noninteracting, and because the excess volumes for similar alkane/aromatic mixtures are very small (Gammon et al., 1993). Equation 1 can also be written in terms of mol fractions of free (x_{free}) and total (x_{total}) alcohols instead of concentration:

$$A_{\text{total}} = l\epsilon_{\text{free}} x_{\text{free}} \rho_{\text{mixture}} + l\epsilon_{\text{H-bonded}} (x_{\text{alcohol}} - x_{\text{free}}) \rho_{\text{mixture}}. \tag{3}$$

Using this equation, x_{free} is calculated from A_{total} for known alcohol loading (x_{total}). Now %H-bonded alcohol is calculated as $100 \times (1 - x_{\text{free}}/x_{\text{total}})$.

Results

Clearly there is spectroscopic evidence for alcohol/aromatic H-bonding. As toluene is added to the 1-hexanol/*n*-hexane mixture, a second H-bonding peak appears and the total peak area increases (Figure 3). A similar trend is also obtained for the case of *m*-xylene, as shown in Figure 4. As the temperature is increased, the free peak is favored, as shown in Figure 5. In both the cases, the aromatic ring is planar, as opposed to "linear" 1-hexanol and *n*-hexane. One might ask if any artifact is seen due to the molecular shapes. To examine this, further experiments were carried out with all ring-type molecules. H-bonding of cyclohexanol/toluene in methylcyclohexane solvent was studied. Here the molecular shapes of toluene and methylcyclohexane were more similar than in the previous case. H-bonding was also observed in this system, as shown in Figure 6. In methylcyclohexane, a single peak due to free cyclohexanol is present. As the toluene concentration was increased, this peak decreased and a new peak due to H-bonding appeared. The combined peak area was much more in toluene than in methylcyclohexane.

Quantitative results of the preceding experiments are shown in Tables 2–4, along with the total peak areas for each experiment. For 1-hexanol/toluene H-bonding, %H-bonding is shown in Figure 7. H-bonding increases as the toluene mol fraction increases, due to increased probability of

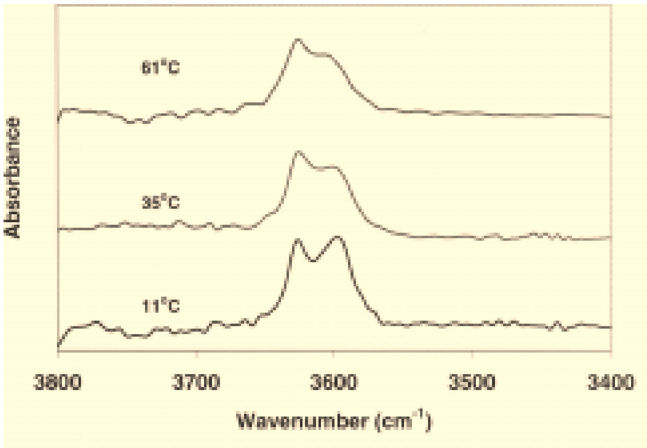

Figure 5. Effect of toluene concentration on the FTIR spectra of cyclohexanol / toluene / methylcyclohexane mixtures, at 11°C.

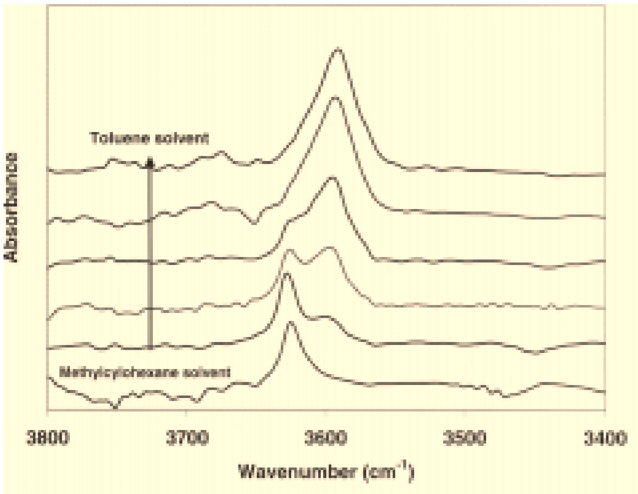

Figure 6. Effect of temperature on the FTIR spectra of cyclohexanol / toluene / methylcyclohexane mixtures.

Table 3. H-Bonding between 1-Hexanol and *m*-Xylene in *n*-Hexane Solvent at 35°C

$x_{m\text{-xylene}}$	x_{alcohol}	$x_{\text{H-bonded}}$	A_{total}
0.00	0.000090	0.000000	0.1565
0.31	0.000089	0.000027	0.2150
0.51	0.000088	0.000044	0.2713
0.77	0.000087	0.000050	0.2831
0.999	0.000086	0.000067	0.3514

Table 4. H-Bonding between Cyclohexanol and Toluene in Methylcyclohexane Solvent

		11°C		61°C	
x_{toluene}	x_{alcohol}	A_{total}	$x_{\text{H-bonded}}$	A_{total}	$x_{\text{H-bonded}}$
0.00	0.000108	0.1344	0.000000	0.1344	0.000000
0.12	0.000105	0.1980	0.000028	0.1278	0.000003
0.34	0.000101	0.2554	0.000052	0.1995	0.000029
0.54	0.000097	0.3249	0.000075	0.2488	0.000047
0.74	0.000094	0.3918	0.000094	0.2735	0.000054
0.999	0.000089	0.3856	0.000089	0.3055	0.000062

donor−acceptor encounters. A similar trend was also observed for *m*-xylene (Figure 8). And, as expected, an increase in the temperature decreased H-bonding, due to higher thermal energies of both donor and acceptor molecules. In the case of cyclohexanol/toluene H-bonding, experiments were performed at two temperatures: 11 and 61°C. Due to the large difference in temperature, there was a large difference in the extent of H-bonding. For the 11°C case, complete H-bonding was reached with only about 70% toluene in the mixture (Figure 8). It is interesting to note that despite the large aromatic-to-alcohol ratio, the %H-bonded alcohol rose rather slowly with increasing toluene concentration. This fact could lead to two hypotheses: that the H-bond between the alcohol and aromatic is fairly weak, and that the H-bond is affected by some steric factor.

Table 2. H-Bonding between 1-Hexanol and Toluene in *n*-Hexane Solvent

		25°C		35°C		45°C	
x_{toluene}	x_{alcohol}	A_{total}	$x_{\text{H-bonded}}$	A_{total}	$x_{\text{H-bonded}}$	A_{total}	$x_{\text{H-bonded}}$
0.00	0.000090	0.1565	0.000000	0.1565	0.000000	0.1565	0.000000
0.34	0.000085	0.2054	0.000023	0.1660	0.000016	0.1811	0.000010
0.55	0.000082	0.2562	0.000038	0.2307	0.000036	0.2165	0.000023
0.74	0.000079	0.2890	0.000047	0.2557	0.000038	0.2371	0.000031
0.999	0.000075	0.3411	0.000056	0.2954	0.000044	0.2610	0.000037

Ab Initio Calculations

In order to obtain a firmer grasp of the magnitude and behavior of the energies involved, a series of rudimentary *ab initio* calculations were performed. For ease of computation, ethanol was substituted for the heavier alcohols examined in the FTIR study. 1-Hexanol or cyclohexanol have many more degrees of freedom compared to ethanol, due to the higher

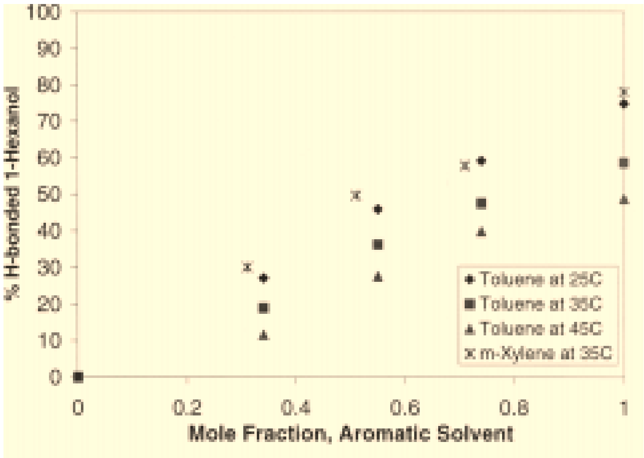

Figure 7. H-bonding between 1-hexanol and aromatic molecule in *n*-hexane solvent.

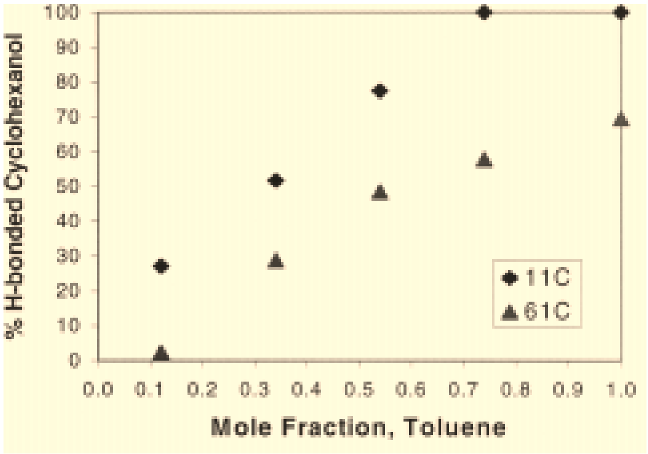

Figure 8. H-bonding between cyclohexanol and toluene in methylcyclohexane solvent.

number of carbon–carbon bonds in the alkyl chain. Choosing ethanol greatly decreases the computational effort required. While these results are not directly comparable to the laboratory data, the relative magnitudes of the results offer some insight into the H-bonding phenomena involved. The calculations were performed using Gaussian 98 (Frisch et al., 1998) on Cray SV1 computer at the Alabama Supercomputer Center. The optimization was done at the Hartree-Fock level with the *6-31(d,p)* basis set. BSSE correction was applied according to the point counterpoise method (Boys and Bernardi, 1970).

Calculations were run for individual molecules and for binary pairs with H-bonding. Results are shown in Table 5 and Figures 9–10. H-bonding energy for ethanol/toluene is −6.6 kJ/mol, and for ethanol/*m*-xylene, it is −7.1 kJ/mol. Interestingly, the *m*-xylene energy is slightly more negative than the bonding energy is for toluene, which is consistent with the FTIR observation of slightly higher H-bonding with *m*-xylene. However, at this level of calculation, the results are not necessarily accurate enough to warrant a concrete conclusion of the energy difference between the two dimers. Alcohol–alcohol H-bonding energy is −25.1 kJ/mol (Panayiotou and Sanchez, 1991), which is much higher than for alcohol–aromatic obtained here. According to the two energies, the equilibrium constant for alcohol–alcohol H-bonding is about 300 times that for alcohol–aromatic, at ambient temperature. Or, in other words, aromatic H-bonds are 300 times weaker than the alcohol self-association. Nonetheless, −6.6 kJ/mol of H-bonding energy is not negligible. This may be the reason why in phase equilibria calculations, aromatic molecules often require adjustable binary parameters to fit the data, using the theories that describe alkane mixtures very

Table 5. *Ab initio* **Energies for Ethanol, Aromatic, and Ethanol/Aromatic Pair Molecules, using Hartree-Fock with the 6-31(*d*, *p*) Basis Set and BSSE Correction**

	Ethanol/Toluene System	Ethanol/*m*-Xylene System
Ethanol molecule	−404.606 MJ/mol	−406.396 MJ/mol
Aromatic molecule	−708.379 MJ/mol	−810.899 MJ/mol
Ethanol/aromatic pair	−1113.033 MJ/mol	−1,215.553 MJ/mol
BSSE correction	−0.041 MJ/mol	−0.041 MJ/mol
H-Bond energy	−6.6 kJ/mol	−7.1 kJ/mol

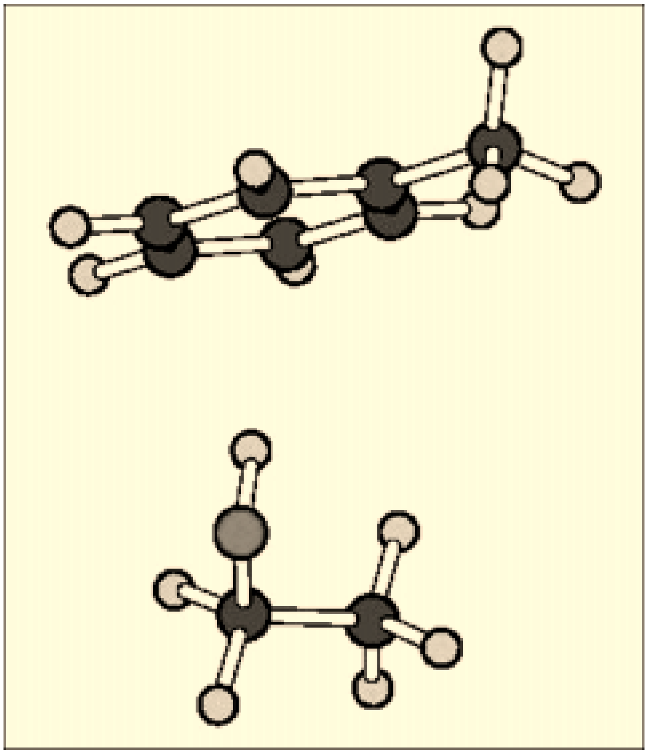

Figure 9. *Ab initio* geometry for optimized ethanol/toluene H-bonded pair.

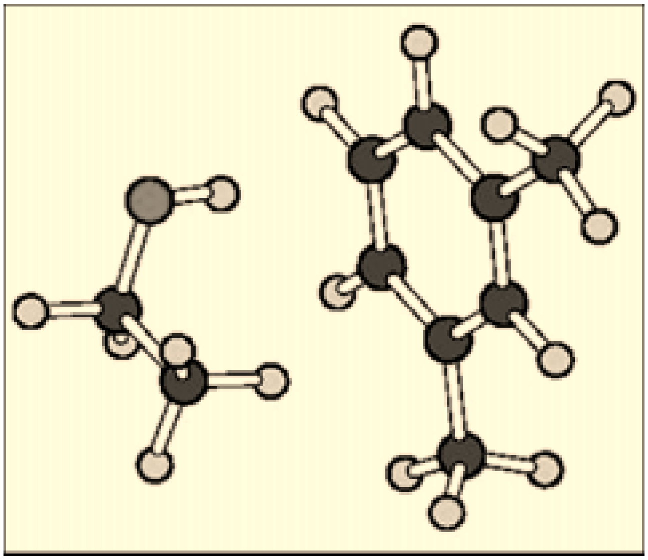

Figure 10. *Ab initio* geometry for optimized ethanol/*m*-xylene H-bonded pair.

well. In addition, in both dimers the respective —OH groups are oriented toward the center of the aromatic ring. This is indicative of the directional characteristic proposed by the experimental results.

Conclusion

FTIR spectroscopy shows that H-bonds can be formed with aromatic rings. H-bonding data are presented for 1-hexanol/toluene, 1-hexanol/*m*-xylene, and cyclohexanol/toluene H-bonding at varying composition and temperature. Both spectroscopy and *ab initio* calculations show that alcohol−aromatic H-bonds are fairly weak H-bonds.

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